



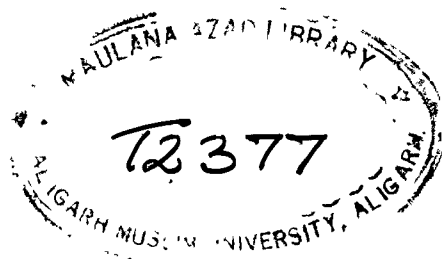
**PHYSICO-CHEMICAL STUDIES ON THE TRANSITION
METAL COMPLEXES OF
NITROGEN CONTAINING LIGANDS**

**THESIS SUBMITTED TO
THE ALIGARH MUSLIM UNIVERSITY, ALIGARH
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY**

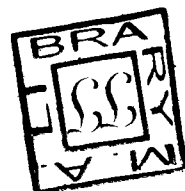
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January, 1981



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Certified that the work embodied in this thesis entitled, "Physico-Chemical Studies on the Transition Metal Complexes of Nitrogen Containing Ligands" is the result of the original researches carried out under my supervision by Mr. Mansoor Ahmad Neyazi and is suitable for submission for the award of the Ph.D. degree of Aligarh Muslim University.


(K. S. Siddiqi).

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Mansoor A. Neyazi
(Mansoor Ahmad Neyazi)

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PUBLICATIONS

1. The synthesis and ligand properties of the dihydrobis(1-indazolyl)borate anion.
S. A. A. Zaidi and M. A. Neyazi; Transition Metal Chem. 4, 164-167 (1979).
2. Tetrakis(1-indazolyl)borate complexes with transition metals.
K. S. Siddiqi, M. A. Neyazi and S. A. A. Zaidi; Synth. React. Inorg. Met.-Org. Chem. (in press).
3. Hydrotris(1-indazolyl)borate complexes of some transition metals;
K. S. Siddiqi, M. A. Neyazi, Z. A. Siddiqi and S. A. A. Zaidi, Indian J. Chem. (communicated).

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ABSTRACT

The virgin field of poly organoborate chemistry emerged only about a decade ago by the pioneering work of Trofimenko who established a series of novel poly(1-pyrazolyl)borates. Following Trofimenko the synthesis of an analogous series of poly(1-indazolyl)borates and poly(5-aminoindazolyl)borates has been done under this project. The transition metal complexes of each member of the series have been studied.

The formation of each member of a series is temperature dependent. When potassium borohydride is mixed with an excess of indazole under molten condition, at 170°C, evolution of two moles of hydrogen occurs. On adding this melt into hot toluene dihydrobis(1-indazolyl)borate is obtained which melts at 245°C. If the above mixture is further heated up to 200°C, a third equivalent of hydrogen is evolved and hydrotris(1-indazolyl)borate, melting at 232°C, is obtained. Finally, on prolonged heating up to a temperature not exceeding 215°C a fourth equivalent of hydrogen is evolved resulting in the formation of potassium tetrakis(1-indazolyl)borate melting at 220°C. This method has been applied for the synthesis of potassium poly(5-aminoindazolyl)borates.

Thus, this method provides a new route for the synthesis of poly organoborates of different composition by varying the temperature.

Potassium dihydrobis(1-indazolyl)borate, synthesized from potassium borohydride and indazole, has been used as a ligand to yield complexes with Cu(II), Ni(II), Co(II), Mn(II), Fe(III), Zn(II), Cd(II) and Hg(II) ions. It has been found to be uninegative and bidentate ligand and coordination is proposed to occur through the nitrogen atom at position 2 of the indazole ring system in all cases. With the sole exception of Cu(II) complex, the nitrogen atom at position 1 is also involved in forming a bridge with an adjacent metal ion. On the basis of electronic spectral studies and magnetic susceptibility measurements a distorted square planar structure involving chlorine bridges has been proposed for Cu(II) complex. An octahedral geometry with ligand bridges for all complexes is tentatively proposed.

Potassium hydrotris(1-indazolyl)borate is the second member of poly(1-indazolyl)borate series. It yields complexes with Cu(II), Ni(II), Co(II), Mn(II), Fe(III), Zn(II), Cd(II) and Hg(II) ions. The complexes have been characterized by elemental analysis, IR., electronic spectral studies and magnetic susceptibility measurements. The molar conductance

of $10^{-3}M$ solution of the complexes suggest them to be non-ionic except for the $Ni[HB(INZ)_3]Cl$ the conductance of which corresponds to 1:1 electrolyte in dimethyl formamide. The Cu(II) complex seems to have a distorted square planar geometry while the others appear to be octahedral.

Potassium tetrakis(1-indazolyl)borate is the third and the last member of the poly(1-indazolyl)borate series. Complexes of this newly synthesized chelate have been prepared with Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) halides. These have been characterized by elemental analysis, IR., reflectance spectral studies, room temperature magnetic susceptibility-, and conductance measurements. All the complexes appear to have an octahedral structure except for the Cu(III) complex. The molar conductance values of $10^{-3}M$ solution of all complexes, except the Ni(II) complex, support nonionic species.

Potassium dihydrobis(5-aminoindazolyl)borate and potassium hydrotris(5-aminoindazolyl)borate have been synthesized from potassium borohydride and 5-aminoindazole at $180^{\circ}C$ and $195^{\circ}C$ respectively. Potassium poly(5-aminoindazolyl)borate has been found to act both as bidentate or a tridentate ligand because of the presence of amino-, pyridyl- and pyrrolic nitrogen atoms.

On the basis of elemental analysis, magnetic susceptibility measurement and electronic spectral studies all the complexes have been proposed to be octahedral although no definite geometry could be proposed for Zn(II), Cd(II) and Hg(II) complexes.

Poly(1-indazolyl)borate, $\left[\text{HnB(InZ)}_{4-n} \right]$ yields only a 1:1 complex with all the metal chlorides by the replacement of only one chloride atom from divalent metal chloride, where the corresponding poly(5-aminoindazolyl)borate yields 1:2 complex, where both of the chlorine atoms of metal chloride are replaced by the ligand.

This obviously indicates that the coordination behaviour of poly(1-indazolyl)borate is different from poly(5-aminoindazolyl)borate.

INTRODUCTION

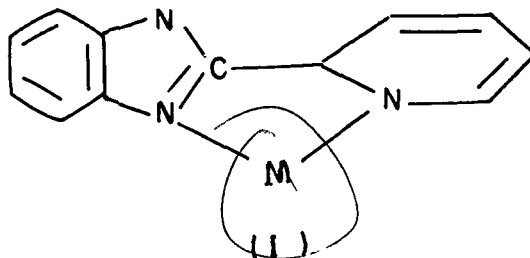
The importance and scope of studies on coordination chemistry of indazole, a derivative of pyrazole could well be assessed from the keen interest shown by many workers and the work appearing in literature during recent years. A brief survey of work on pyrazole and imidazole will, therefore, be helpful in bringing out the importance and the scope of this project.

During recent years the coordination chemistry of imidazole and pyrazole has assumed much importance owing to the fact that imidazole and its substituted derivatives have been found to be of considerable biological significance. They play crucial role in the structure and functioning of a number of biologically important molecules by virtue of their being coordinated to metal ions. Thus dimethyl benzimidazole supplies one of its nitrogen atoms to cobalt(III) for coordination in vitamin B₁₂ in several of its derivatives¹, and there is strong evidence that in proteins containing "heme" as possible prosthetic group, eg., hemoglobin, myoglobin, cytochrome C, imidazole nitrogen atoms, in histidine residues

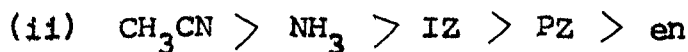
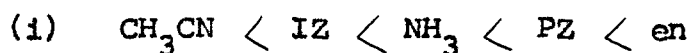
of the proteins, are coordinated to the iron atoms^{1,2}. Histidine units can function as buffering groups as in the hemoglobin oxyhemoglobin systems^{3,4}. Insulin hexamer is reported to have two zinc ions, each bound to imidazole of three histidine units^{3,5}. Cytochrome C has an iron ion coordinated with a porphyrin ring and a histidine unit along with the sulfur of a methionine^{3,6}. The possibility of the use of imidazole complexes as anti-tumor drug⁷ has recently been reported.

The coordination compounds of pyrazole, imidazole and their substituted derivatives with first row transition metals are well documented. The complexes of second row transition metals with these ligands have not been thoroughly investigated except for a few metal complexes of imidazole, benzimidazole, pyrazole, dimethyl pyrazole and 2(2'-pyridyl) benzimidazole which have been recently described⁷⁻¹⁴.

Ghosh and coworkers¹³ have reported the preparation and properties of Co(II), Co(III), Ni(II), Cu(II), Pd(II), Rh(III), Ir(III) and Pt(II) complexes with 2(2'-pyridyl) benzimidazole, a ligand which behaved as a bidentate one coordinating through the pyridyl nitrogen and tertiary nitrogen of the imidazole ring.



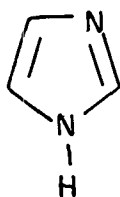
Pyrazole is placed in the spectrochemical series (with increasing Dq) and nephelauxetic series (with decreasing B) respectively under (i) and (ii) below¹⁵.



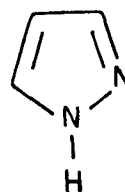
where IZ is imidazole and PZ is Pyrazole. Even though pyrazole is a weaker base than imidazole ($\text{pK}_a = 2.47$ c.f. 6.95 for imidazole) it forms well defined complexes with transition metals¹⁶⁻²¹. A general formula reported for the pyrazole complexes is $\text{M}(\text{PZ})_n\text{X}_m$ where $\text{M} = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$ and Cd(II) , PZ is monohapto-pyrazole ligand and X is the anion, Cl^- , Br^- , SCN^- , BF_4^- , NO_3^- , SO_4^{2-} , and ClO_4^- , $n = 2-6$. Similar type of imidazole complexes have also been isolated²²⁻²⁷. The number of pyrazole or substituted pyrazole²⁸⁻³¹ molecule coordinated to the metal

ions depends on the nature of the metal ion itself, the counter ion and the size of the substituted pyrazole nucleus. Pyrazole forms tetrakis complexes with the halides of Ni(II), Co(II) and Fe(II)³²⁻³³. However, with Cu(II) halides bis pyrazole complexes were obtained^{34, 35}.

Since indazole is a derivative of pyrazole, a description of the latter compound will be appropriate. The coordination chemistry of pyrazole has been compared with that of imidazole, although the complexing behaviour of imidazole (IIA) is well documented in literature. Comparatively less information is available regarding the metal complexes of pyrazole (IIB).



(I I A)

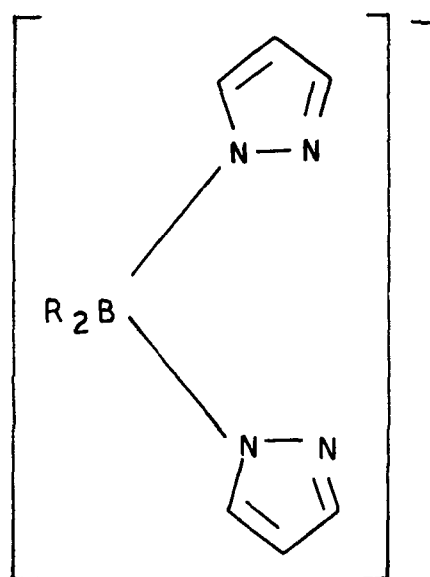


(I I B)

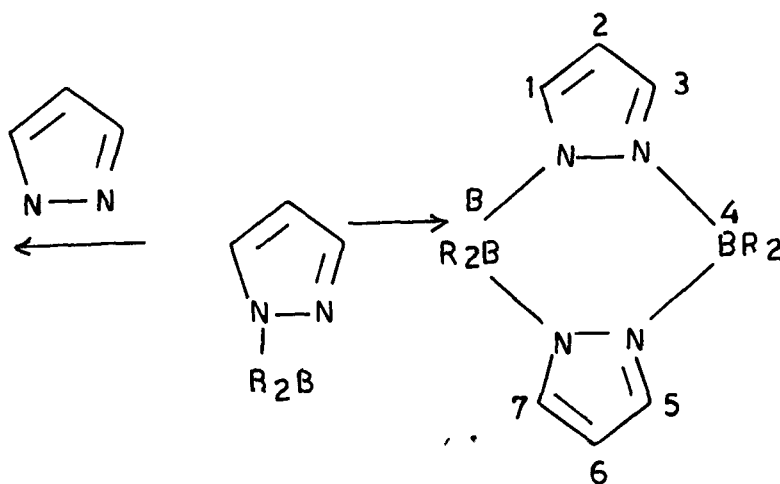
Boron-pyrazole chemistry which deals with the compounds containing boron bonded to nitrogen of a pyrazole nucleus, is a new and fertile field of remarkable scope for

chemical research³⁶. It has yielded novel classes of boron heterocycles chelating ligands, and transition metal compounds.

Such versatility stems from the singular combination of electronic and geometric features of the 1-boryl pyrazole fragment that leads to its facile stabilization either through dimerization or through coordination with a pyrazolide ion³⁷. In this manner structure (IIIA) and (IIIB) respectively are produced. They are representatives of two main sub areas of boron pyrazole chemistry.



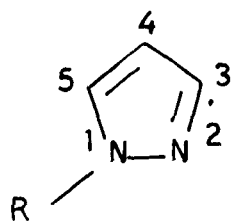
(IIIB)



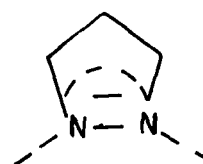
(IIIA)

The poly (1-pyrazolyl)borate ligand $[\text{HnB(PZ)}_4]^-$ was first reported by Trofimenko³⁸, since then a wide variety of group II and d-block transition metal complexes of the ligand have been described³⁹. Most of the latter are derived from metals in the oxidation state (II). The series of these complexes with divalent transition metal ions is of particular interest since these ligands offer the opportunity of forming chelates of the same metal ion with different geometries. The n.m.r., magnetic susceptibility and electronic spectral data are described for complexes containing Mn^{2+} , Fe^{2+} , Co^{2+} , Cu^{2+} and Zn^{2+} ions, both the complexes with bidentate and tridentate ligands have been examined and physical evidence presented suffices to characterize their geometries⁴⁰.

The pyrazole nucleus, (IVA) is thermally and hydrolytically very stable. As a ligand, it coordinates to metals and metalloids through 2-N, as do 1-alkylpyrazoles. When deprotonated, pyrazole becomes the pyrazolide ions, (IVB), which can coordinate through both nitrogen atoms as an exobidentate⁴¹ ligand of C_{2v} symmetry.



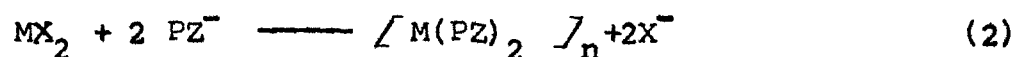
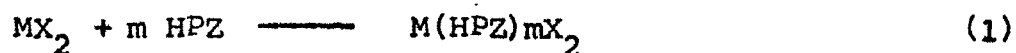
(IV A)



(IV B)

The nucleophilicity of the nitrogens and their steric accessibility may be varied through appropriate ring substitution⁴²⁻⁴⁶.

A general formula, $M(HPZ)_n X_m$ for typical pyrazole complexes has been suggested where M is a transition metal, HPZ is a 2-monohaptopyrazole ligand, X is the counterion, and m is the valence of the transition metal, usually 2. These complexes are readily prepared by the reaction of metal salts with pyrazole or their derivatives in neutral or slightly acidic media, to prevent the formation of pyrazolide polymers, $[M(PZ)_2]_n$, which predominates under basic conditions



The number of pyrazole molecules coordinated to a metal ion depends on a number of factors.

(1) Coordinating ability of the counterion : Maximum number of pyrazole molecules coordinated to a metal ion does not exceed six in a complex of the type $M(HPZ)_6 X_2$ where X is NO_3 , BF_4 and $M = Mg, Mn, Fe, Co, Ni, Zn$ or Cd ⁴⁷⁻⁴⁸. Complexes of the type $M(HPZ)_4 X_2$ are formed when X is a halide ion and $M = Ni(II), Co(II)$ and $Fe(III)$ ⁴⁷.

(2) Nature of the metal ion: Hexakispyrazole

copper(II) complex could not be prepared under any conditions. However it yielded only a tetracoordinate complex, $\text{Cu}(\text{HPZ})_4\text{X}_2$, irrespective of the nature of X (Cl, Br, BF_4 , ClO_4 , SO_4 , NO_3)^{47,49-51}. Furthermore, $\text{Cu}(\text{HPZ})_2\text{Cl}_2$ was also obtained which is similar to $\text{Cu}(\text{H } 3,5\text{-Me}_2\text{PZ})(\text{OAc})_2$ ⁵¹.

(3) Substitution on the pyrazole ring: A substituent

introduced at position 3 in the pyrazole ring produces steric hindrance and makes it difficult to have such six 3-substituted pyrazole molecules coordinated via the 2-N to a metal. In fact, the highest apparent coordination number for a variety of transition metal ions (Mn, Fe, Co, Cd) has been reported⁵⁰.

Electronic spectra of $\text{Ni}(\text{HPZ})_6^{2+}$ recorded in solution⁴⁷ or in solid state⁵² gave ligand field Dq values of 1065-1080 cm^{-1} indicating that pyrazole occupies a position similar to that of pyridine or ammonia in the spectrochemical series. 3(5)-Methylpyrazole, which has an electron releasing group should be stronger coordinating ligand. This is also exhibited by the ligand field and magnetic parameters of the complexes prepared from $\text{H}_3(5)\text{MePZ}$ and various divalent metal salts^{50,53}.

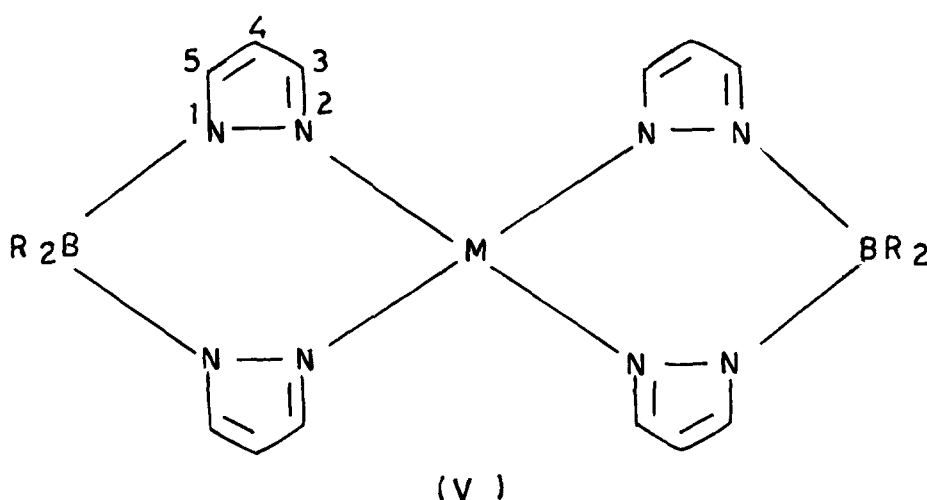
In a study of selective extraction of transition metal ions into an organic phase from acidic aqueous solutions through complex formation with various 1,3,4,5-tetraalkyl- and 3,4,5-trialkylpyrazole, it was shown that Fe(III), Zn(II), Cd(II) and Co(II) can be successfully extracted throughout the acidic range while optimum extraction for other ion is strongly pH dependent⁵⁴. In addition to complexing with simple transition metal ions pyrazoles have been reported to be coordinated to diverse organometallic species.

A unique interesting class of pyrazole-based ligands are geminally poly(1-pyrazolyl)-substituted compounds. Of these, the uninegative poly(1-pyrazolyl)borates, $\left[\text{RnB(PZ)}_{4-n} \right]^-$ have been studied in some detail. In principle, elements other than boron or carbon may serve as the site of poly-substitution with 1-pyrazolyl groups. The charge on such a ligand will depend on the nature of the element and the number of pyrazolyl groups linked to it.

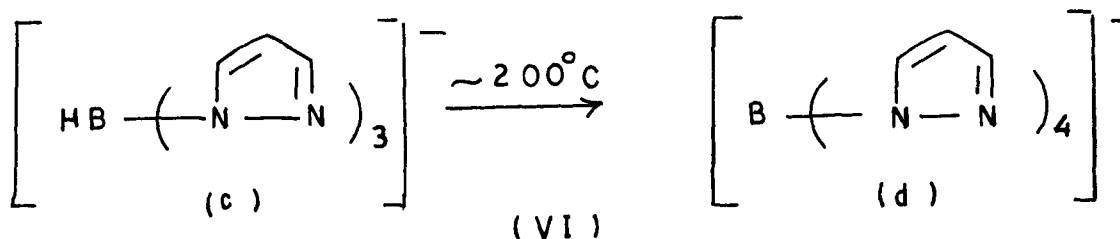
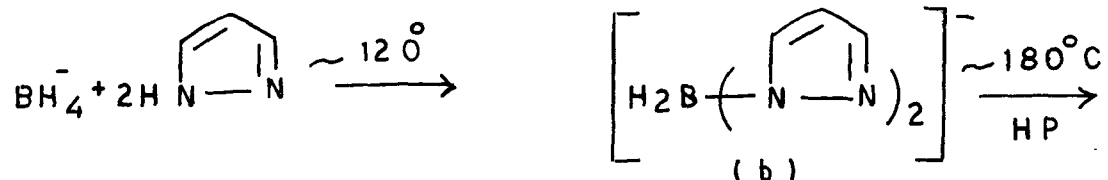
A. Poly(1-Pyrazolyl)borates:

The coordinating ability of a poly(1-pyrazolyl)borate ion, $\left[\text{RnB(PZ)}_{4-n} \right]^-$ is a consequence of favourable electronic and geometric factors. A dipyrazolyl borate ion, $\text{R}_2\text{B(PZ)}_2^-$, resembles a 1,3-diketonate ion and forms chelates

with divalent transition metal ions. The nitrogen atoms are fully coordinated in this case and thus unavailable for further coordination, since the area around the metal is screened by substituents in the 3 position. Consequently, chelates are, in contrast to 1,3-diketonates (always monomeric).



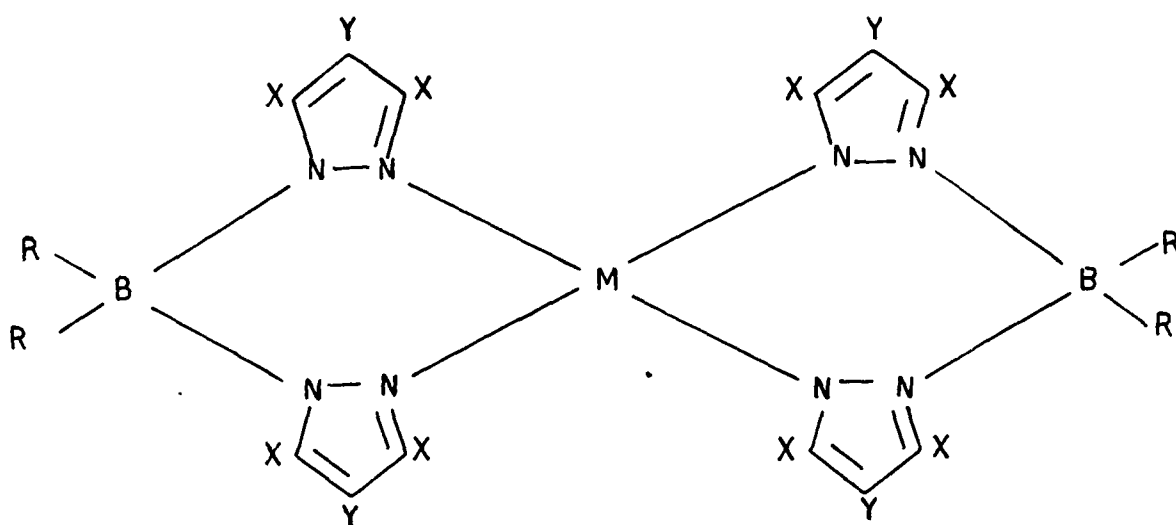
The parent ligands (b), (c) and (d) are obtained by the reaction of an alkali metal borohydride on pyrazole where the extent of substitution depends on the reaction temperature^{55,56}. These salts, unlike any other BR_4^- species, yield on acidification isolable and stable free acids. These may be converted via neutralization with NR_4OH to organic-soluble quaternary ammonium salts unavailable by the direct synthetic route.



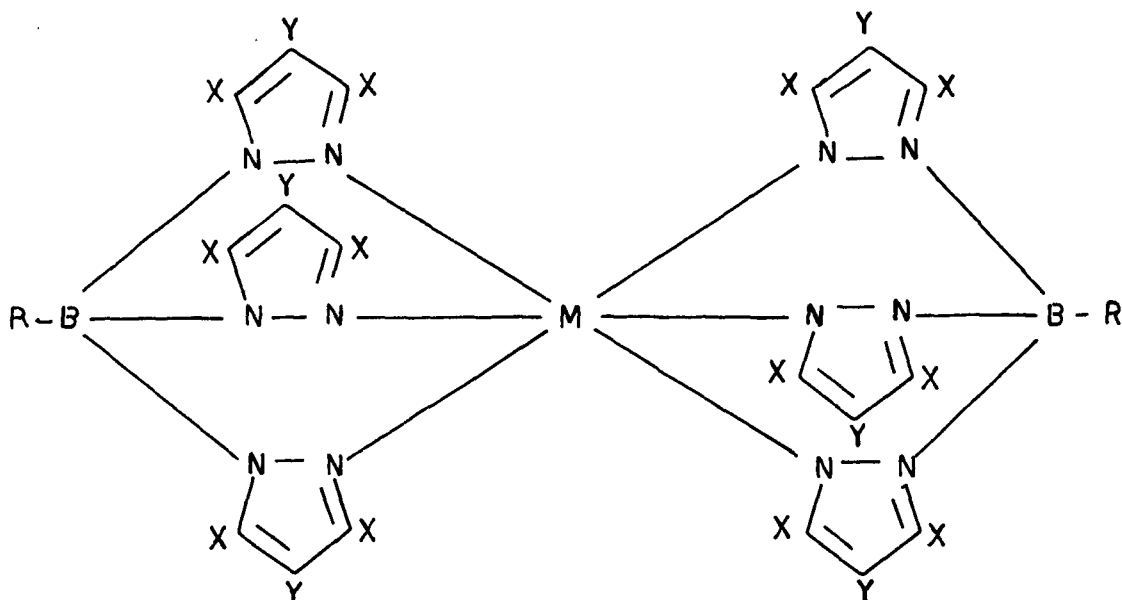
The parent bidentate ligand, $\text{H}_2\text{B}(\text{PZ})_2^-$, forms monomeric chelates, $\left[\text{H}_2\text{B}(\text{PZ})_2 \right]_2\text{M}$, with most divalent first row transition metal ions. These organic-soluble and sublimable compounds are air stable, except for the Fe(II) and Mn(II) derivatives⁵⁷. The isomorphous Ni and Cu chelates are square planar, while those of Mn, Fe, Co and Zn are tetrahedral. This assignment rests on optical spectra, magnetic measurement and n.m.r. data⁵⁸.

The complexes fall into two general categories. It has been shown that in the first of these the bis(1-pyrazolyl) borate unit behaves as a bidentate chelating ligand and that the resulting compounds have structure of type (VIIA) where

$R = H$, alkyl, or aryl, and the pyrazolyl residues may contain substituents. Trofimenko et al adopted the convenient abbreviation $M [R_2B(PZ)_2]_2$ for these compounds. These were shown to have either an essentially planar configuration about the metal ion (Ni^{2+} , Cu^{2+}) or an essentially tetrahedral array (Mn^{2+} , Fe^{2+} , Co^{2+} and Zn^{2+}).



(VII A)

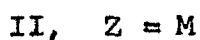
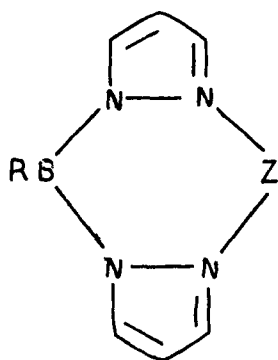


(VII B)

In the second class, (tridentate) ligands are involved, as exemplified by structure (VIIB) and this structure occurs with all six metals and may be represented as $M[RB(PZ)_3]_2$. The tridentate ligands give rise to octahedral complexes⁵⁸.

Trofimenko suggested^{38,59} that when a BR_2 group acts as a bridging unit between two pyrazole nuclei, several new classes of compounds of boron are obtained, depending on the nature of the second bridging unit⁶⁰. When this unit, Z, is BR_2 , the resulting structure is a pyrazabole, VIII(I) and

when it is a metal or an onium ion, the compound belongs to the class of poly(1-pyrazolyl)borates, VIII(II), it belongs to the class of uninegative tetrasubstituted boron compounds which hitherto have been known only as salts. Of these, there are only a few examples $[BRnR'_{4-n}]^-$ species containing a B - N band, N being an amino, pyrrolyl or indolyl group. None of these has displayed an unusual properties^{56,61-65}.



VIII

Trofimenko has suggested the method of synthesis of the two parent ligands, dihydrobis(1-pyrazolyl)borate⁵⁶ and hydro tris(1-pyrazolyl)borate and derived their free acidic

and their chelates. Although tetrakis(1-pyrazolyl)borate⁵⁶ is, in terms of coordinating ability merely a substituted variant of tris(1-pyrazolyl)borate, but fits in the $[H_nB(PZ)_{4-n}]^-$ formula.

The oxidative and hydrolytic stability of poly (1-pyrazolyl)borate increases with decreasing number of hydrogen attached to boron. Thus $H_2B(PZ)_2^-$ is oxidized instantaneously by aqueous permanganate.

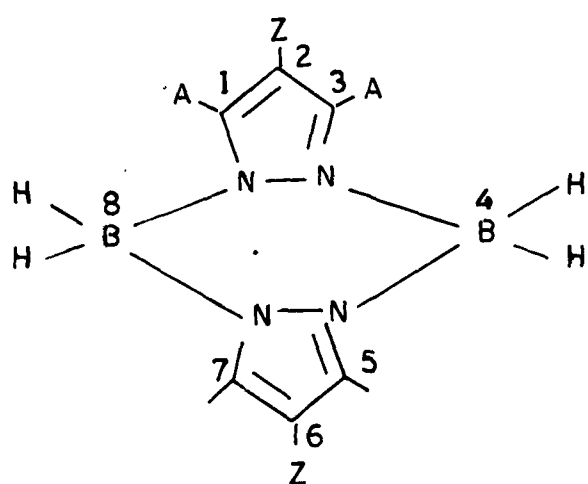
The oxidative and hydrolytic stability of poly (1-pyrazolyl)borate increases with decreasing number of hydrogen attached to boron. Thus $H_2B(PZ)_2^-$ is oxidized slowly, while $B(PZ)_4^-$ remains unaffected under these conditions. This trend is also corroborated by polarographic studies. The same order of stability is observed with regard to storage of their solution, $B(PZ)_4^-$ can be stored for long periods of time in solution without noticeable deterioration, while $HB(PZ)_3^-$ is stored less well and $H_2B(PZ)_2^-$ solution have to be used within a few days of their preparation. In the solid state, however, all three salts can be stored for years at room temperature exposed to air and light.

Coordination compounds derived from $\text{H}_2\text{B}(\text{PZ})_2^-$, $\text{HB}(\text{PZ})_3^-$, $\text{B}(\text{PZ})_4^-$, and divalent first row transition metal ions can be prepared readily by metathesis.

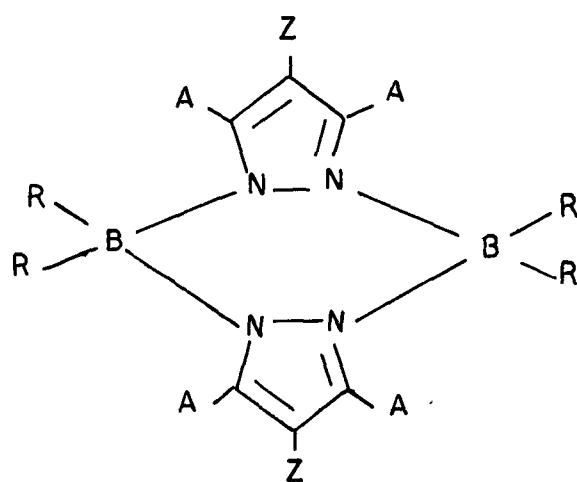
Chelates of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} are precipitated immediately when aqueous solution of $\text{KH}_2\text{B}(\text{PZ})_2$ and the appropriate metal ions are mixed. Similarly, the compounds, $\text{M}[\text{H}_2\text{B}(\text{PZ})_2]_2$ are precipitated when M is Pb^{2+} or Cd^{2+} , but not when M is Mg^{2+} , Ca^{2+} , Sr^{2+} or Ba^{2+} , Ag^{2+} , Pd^{2+} and Hg^{2+} ions which are reduced to the free metals. Compounds $\text{M}[\text{H}_2\text{B}(\text{PZ})_2]_2$ are extractable with organic solvents, particularly well with methylene chloride.

Pyrazaboles(1) are a novel class of remarkably stable boron heterocycles^{38,48}. In the first paper of this series the synthesis and properties of pyrazaboles of structure VIII(I) and VIII(II) were described. These compounds were obtained by the reaction of appropriately substituted pyrazoles with boron complexes or with trialkyl or triaryl boranes respectively. Although widely applicable, such a synthetic approach, henceforth referred to as "direct synthesis" still had some limitations. Here it is concerned with two aspects of pyrazabole chemistry:

- a) Substitution Chemistry of pyrazaboles, and
- b) Chemical transformation of functionally unsubstituted pyrazaboles which maintain the intact ring system⁶⁶.



(IX A)



(IX B)

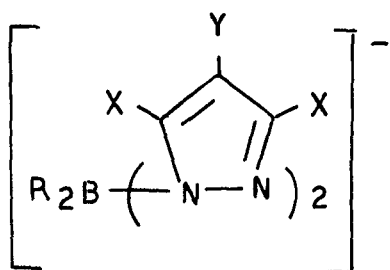
R = alkyl, aryl

A = H, alkyl, aryl, halogen

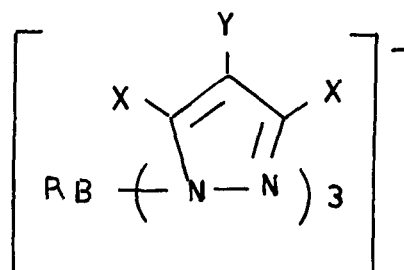
Z = H, R, NO₂, CN, halogen.

In the boron-pyrazole chemistry area, it was described to determine the effect of the presence of diverse substituents on carbon or boron on the properties of transition metal poly(1-pyrazolyl)borates and, to devise synthetic approaches to such compounds. They considered, in

term (A) bidentate ligands containing substituents on carbon(Ia) or boron (Ib) and the chelates derived there from and (B) tridentate ligands with substituents on carbon (IIa) or boron(IIb) and their compounds with transition metals⁶⁷.



(X)



(XI)

Ia, R = H; X and/or Y ≠ H

Ib, R ≠ H; X = Y = H

IIa, R = H; X and/or Y ≠ H

IIb, R ≠ H; X = Y = H

Boron-indazole chemistry which deals with compounds containing boron bonded to nitrogen of an indazole nucleus is a new field and offers several areas of study. It has

yielded boron heterocycles, chelating ligands and transition metal compounds. This provides a new modified route for the preparation of poly(1-indazolyl)borates and poly(5-aminoindazolyl)borates of different composition by varying the temperature.

This peculiar behaviour arises from the singular combination of electronic and geometric features of the 1-boryl indazole fragment that leads to its facile stabilization either through dimerization or through coordination with an indazole ion.

The chemical literature reveals that most of the work carried out on boron chemistry is concerned with the synthesis of a novel class of ligand of the type $[HnB(PZ)_{4-n}]$ where PZ = pyrazole and their complexes with first row transition metal ions. In extending the work on boron-indazole chemistry area it was desirable to devise synthetic approaches to poly(1-indazolyl)borate and poly(5-aminoindazolyl)borate and a study of their complexes with transition metal ions.

All possible boron derivatives of indazole and 5-aminoindazole have been synthesized by a known but modified technique, controlling the reaction temperature.

EXPERIMENTAL METHODS

Several Physico-chemical methods are available for the study of coordination compounds. The techniques used for the investigation of the structure of newly synthesized compounds described in the present work are as under:

1. Infra-red spectra
2. Ultra-violet and visible (ligand-field) spectra
3. Magnetic susceptibility
4. Molar conductance

It will, therefore, be quite appropriate to describe these technique in detail.

Infrared spectra:

Infrared spectroscopy is a very useful technique for ascertaining the coordination site and bonding in the complexes.

The infrared region extends from $25\ \mu$ to $15\ \mu$ (4000 to $667\ \text{cm}^{-1}$). The region from $0.8\ \mu$ to $2.5\ \mu$ ($12,500$ to $4000\ \text{cm}^{-1}$) called the near infrared region and that from

15 μ to 200 μ (667 to 50 cm^{-1}) is called the far infrared region. The compound whose spectrum is to be recorded may be solid, a liquid or a gas. The spectrum of a solid can be examined either in nujol or in Hexachlorbutadiene or KBr. The infrared frequencies are determined by the mechanical motion in the molecule while the intensities are related to electrical properties.

Various stretching and bending vibrations of a bond occur at certain quantized frequencies. When infrared light of the same frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased when the molecule reverts from the excited state to the original ground state, the absorbed energy is released as heat.

A non-linear molecule that contains n atoms has $3n-6$ possible fundamental vibrational modes. Sometimes these vibrational modes are less than the expected number. Since the absorption of electromagnetic radiation in i.r. region is possible only when there is a change in the dipole moment of the molecule during the normal vibration if there is no such change, it will be "infra red inactive". The occurrence or non occurrence of an infra red radiation is governed by the following rules.

i) In order to a molecule to absorb infra red radiation as vibration excitation energy, there must be a change in the dipole moment of the molecule as it vibrates.

ii) In absorption of radiation only transitions for which change in the vibrational energy level is $V = +1$, can occur, since most of the transitions will occur from the state V_0 to V_1 , the frequency corresponding to this energy is called the fundamental frequency.

While the complete normal coordinate analysis of a given molecule is necessary for prediction of all the bands in its I.R. spectrum, it is at times enough to consider the frequencies of certain group of atoms called "Group frequencies". These frequencies are characteristic of the groups, irrespective of the nature of molecule to which these groups are attached. The absence of any band in the appropriate region indicates the absence of that particular group in the molecule. Not all the vibrational frequencies however, are group frequencies. Each molecule undergoes vibrations which are characteristic of the molecule as a whole and are strongly dependent upon the geometrical arrangement in the space and the kind and masses of the molecule's constituent atoms. Such frequencies are called as fingerprint frequencies.

In addition to the group frequencies and fingerprint or characteristic frequencies, a spectrum of a substance shows overtone and combination absorption, which arise from multiples of fundamental frequencies. These absorptions are generally weaker than the fundamental frequencies. In the following paragraphs the characteristic frequencies which are required for the discussion of the compounds described in this work will be discussed.

N - H Stretching: The N-H Stretching vibrations occur in the region $3500 - 3300 \text{ cm}^{-1}$ in dilute solutions⁶⁸. The N-H stretching band shifts to lower value in the solid state due to extensive hydrogen bonding. Primary amines in dilute solutions, in nonplar solvent give two absorption bands in the above mentioned region, the first of which due to symmetric stretch is usually found near 3500 cm^{-1} and the second which corresponds to asymmetrical modes is found near 3400 cm^{-1} . These bands are usually $125-150 \text{ cm}^{-1}$ apart. Secondary amines show only a single N-H stretching in dilute solutions. The N-H band in pyrrole occurs at 3488 cm^{-1} and the frequency range for substituted pyrroles has been found to be $3435-3400 \text{ cm}^{-1}$.

N - H Deformation: For the deformation frequencies of the NH_2 group in Primary amines four characteristic peaks

should appear, but the only definite assignment has been done in the case of scissoring vibrations, generally observed in the region $1650-1590\text{ cm}^{-1}$ ⁶⁹. The lower frequency deformation vibrations of the NH_2 group have not been investigated in detail. The NH_2 twisting, Wagging and torsional vibrations in methylamine have, however, been assigned to 1455 , 780 and 265 cm^{-1} respectively.

C - H Stretching Vibrations: The C-H stretching frequencies are found in the range $3100-3000\text{ cm}^{-1}$ ⁶⁸. In aromatic compounds C-H absorption bands have been found in the region 3038 cm^{-1} . Many monosubstituted aromatic compounds show a characteristic triplet of this type at about 3058 cm^{-1} in carbon tetrachloride solution, but there are some times more bands than this. In nearly all the cases, however, one band is stronger than others. Pyridine shows C-H absorption band in the range $3070-3020\text{ cm}^{-1}$ which appears as a series of multiple absorptions under high resolution⁷⁰. The position and number of these bands vary with the substituents involved.

B - H Stretching Frequency: The BH_2 stretching absorption give rise to strong band in the region $2230-2460\text{ cm}^{-1}$ and BH stretch appeared as a single peak at about 2470 cm^{-1} .

C - H in Plane and out of plane Deformation: A number of characteristic absorption bands in the region 1250-1000 cm^{-1} are exhibited by most of the heterocyclic compounds and are attributed to C-H in plane deformation bands⁷¹. Bands appearing in the region 900-700 cm^{-2} have been attributed to the C-H out of plane deformation vibrations and the position of these bands depends on the number of free hydrogen atoms adjacent to one another⁷².

C = C and C = N Stretchings: These frequencies occur from 1700-1575 cm^{-1} . The C = N absorption in open-chain system or in non conjugated systems occurs within the range 1690-1640 cm^{-1} but in conjugated ring systems, both C = C and C = N stretching bands are present⁷³. Therefore, the identification of C = N absorption is difficult due to interaction with C = C. Pyridine shows a C = N absorption band at 1580 cm^{-1} .

C - N Stretching Frequency: The C - N stretching absorption gives rise to strong bands in the region 1350-1250 cm^{-1} in all the amines⁷⁴. In aromatic primary amines there is one band in the region 1340-1250 cm^{-1} but in secondary amines two bands have been found in the region 1350-1280 cm^{-1} and 1280-1230 cm^{-1} .

M - N Stretching Frequency: The M - N stretching frequency is of particular interest since it provides direct information regarding the coordinate bond. It appears in the low-frequency region. The M-N stretching frequency depends on the following factors:

- i) Mass of the metal and ligand.
- ii) Oxidation number of metal ion.
- iii) Coordination number of metal ion.
- iv) Geometry of the complex.
- v) Basicity of the ligand molecule.
- vi) Bridging or non-bridging anions.
- vii) Ligand field stabilization energy.

M - X Stretching Frequency: The most widely investigated and probably the best understood aspect of the work on metal ligand vibration is that on metal-chlorine systems and to a lesser extent, metal-bromine and metal-iodine systems. Most of these frequencies lie below 400 cm^{-1} region. Apart from the simple halide ions the commonest ligands are those in which the donor atom is carbon, nitrogen or oxygen. The vibrational frequencies associated with M-O, M-C and M-N bands cover large ranges which extend into the low frequency regions. Ligands involving non first row element

donor atoms (such as P, As, Sb, S, Se and Te) usually require low frequency measurements for location of the modes associated with metal ligand skeleton. The presence of the heavier atom in the ligand also gives rise to the low frequency ligand bands.

Metal-halogen stretching frequencies generally increase as the oxidation number of the metal increases. This might be expected on the grounds that, the greater the positive charge on the M ion, the nearer the negative X ion can approach and the more it will be polarized, thus leading to greater covalent character of the M-X bond. Lewis et al. have studied the complexes of the type $[M(III)D_2Cl_2]^+ ClO_4^-$ and $M(III)D_2Cl_2$ $[M = Fe, Ru, Te, Os, Re; D = O\text{-phenylene-bis dimethyl arsine}]$. The infrared antisymmetric metal-chlorine stretching frequencies were observed at 373, 349 cm^{-1} ; 340, 316 cm^{-1} ; 343, 304 cm^{-1} ; 322, 288 cm^{-1} ; 325, 279 cm^{-1} respectively, suggesting that the metal halogen stretching frequencies increase as the oxidation number of the metal increases.

Woodward and Taylor⁸² have measured the totally symmetric stretching frequencies for $InCl_4^-$ (321 cm^{-1}); $InCl_5^{2-}$ (295 cm^{-1}); $InCl_5^{3-}$ (275 cm^{-1}), suggesting that for a given oxidation state of a metal, the metal halogen stretching

frequencies decrease as the coordination number of the metal ion increases.

It has been found that the metal halogen stretching frequencies depend on the mass M , as the mass of the metal M increases the stretching frequencies will tend to decrease. In the complexes of the type $M(II)D_2Cl_2$ [$M = Fe, Ru, Os$], the $Fe - Cl$, $Ru - Cl$, $Os - Cl$ stretching modes were observed at 349, 316, 288 cm^{-1} respectively, suggesting that there is a decrease in the $M-Cl$ stretching frequency (cm^{-1}), on passing down the group. Similarly, for the $[M(III)D_2Cl_2]^+ ClO_4^-$ complex, the $M-Cl$ stretching mode decreases in order $Co-Cl$ (388 cm^{-1}), $Rh-Cl$ (358 cm^{-1}) and $Ir-Cl$ (335 cm^{-1})⁷⁵. In the square planar $Rh(I)$ and $Ir(I)$ complexes, $Rh(Co)Cl(PPh_3)_2$ and $Ir(Co)Cl(PPh_3)_2$, $Rh-Cl$ and $Ir-Cl$ stretching modes were observed at 309 cm^{-1} and a pair at 317 cm^{-1} and 311 cm^{-1} , respectively, suggesting that some bond strengthening might occur on passing from Rh to Ir , in these system⁷⁶.

In the halogen bridged molecules of the type M_2X_6 , in which the metal atoms have a square planar configuration, four stretching modes mainly associated with the bridging MX system and four mainly associated with the terminal $M-X$ group are observed. The best known examples of ions of this type are the $[Pt_2X_6]^{2-}$ and $[Pd_2X_6]^{2-}$ systems, where $X =$

Cl, Br and I. Adams et al,⁷⁷ have analysed the infrared spectra of such system and on rough calculation, found that the M-Cl bridge bond stretching force constants ranged from 75-100% of those for the terminations. It has been suggested by Adams and Churchill⁷⁸ that, in the square planar systems, the sharing of an edge results in little distortion of the metal-metal distance, whereas, if the two tetrahedra share an edge the metal atoms are brought more closely together which leads to electrostatic repulsion and a consequent lengthening of the bridge bonds.

Complexes of the type $Rh_2X_2L_4$, in which a square planar bridge is involved, have been investigated by Adams and Chandler⁷⁹. In these systems the spectra are not complicated by terminal Rh-Cl frequencies and the assignment is thus reasonably certain.

The complexes $KCuCl_3$, NH_4CuCl_3 and $LiCuCl_3 \cdot 2H_2O$ all contain the planar $[Cu_2Cl_6]^{2-}$ ion. Adams and Lock⁸⁰ have assigned the terminal bridging frequencies in these species and found that the two terminal modes lie very close together. In the complex $Cu_2X_4 [Pyridine-1-oxide]_2$, the four halogens are all in terminal position, the copper atoms being bridged by the pyridine-1-oxide molecule. In this complex a single band at 315 cm^{-1} with a shoulder at

325 cm^{-1} must be due to the terminal Cu-Cl stretching frequency. This strongly supports the assignments of the higher frequency band in $[\text{Cu}_2\text{Cl}_6]^{2-}$ to the Cu-Cl terminal stretch⁸¹.

Ultraviolet and Visible (Ligand-field) Spectra:

Most of the compounds absorb light some where in the spectral region between 200 and 1000 nm. These transitions correspond to the excitation of electrons of molecules from ground state to higher electronic state. While ultraviolet and visible spectra of organic molecules have been extensively studied, the application of ligand field spectra to coordination chemistry has come into fashion relatively recently. In a transition metal all the five 'd' orbitals viz. d_{xy} , d_{yz} , d_{xz} , d_{z^2} and $d_{x^2-y^2}$ are degenerate. However, in coordination compounds due to the presence of ligand, this degeneracy is lifted and d orbitals split into two groups, called t_{2g} (d_{xy} , d_{yz} and d_{xz}) and e_g (d_{z^2} and $d_{x^2-y^2}$) in an octahedral complex and t and e in a tetrahedral complex. The set of t_{2g} orbital goes below and the set of e_g orbital goes above the original level of the degenerate orbitals in an octahedral complex. In the case of tetrahedral complexes the position of the two sets of orbitals is reversed, the e set going below and the t set going above

the original degenerate level. When a molecule absorbs energy equal in magnitude to $h\nu$ (where h is the planck's constant and ν is the frequency of radiation) which is sufficient to cause electronic transitions, the electrons are excited from the ground to the excited state.

In order to interpret the spectra of transition metal complexes, the device of energy level diagram based upon 'Russell-Saunders Scheme' must be introduced. This has the effect of splitting the highly degenerate configuration into groups of levels having lower degeneracies known as "term symbols".

The orbital angular momentum of electrons in a filled shell vectorially add up to zero. The total orbital angular momentum of an incomplete 'd' shell electrons is obtained by adding L values of the individuals electrons, which are treated as a vector with the component ' m_l ' in the direction of the applied field, thus

$$L = \sum_i m_{l_i} = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$$

S P d F G H I

The total spin angular momentum $S = \sum_i S_i$ where S_i is the value of spin angular momentum of the individual elec-

trons. 'S' has a degeneracy equal to $2S + 1$, which is also known as "spin multiplicity". Thus a term is finally denoted as " γ_L ". For example, if $S = 1$ and $L = 1$ the term will be 3_P and similarly if $S = 1\frac{1}{2}$ and $L = 3$ the term will be 4_F .

In general the terms arising from a d^n configuration are as follows:

d^1	d^9	2_D
d^2	d^8	$3_F, 3_P, 1_G, 1_D, 1_S$
d^3	d^7	$4_F, 4_P, 2_H, 2_G, 2_F, 2_D(2), 2_P$
d^4	d^6	$5_D, 3_H, 3_F(2), 3_D, 2_P(2), 1_I, 1_G(2), 1_F$
		$1_D(2), 1_S(2)$
d^5		$6_S, 4_G, 4_F, 4_D, 4_P, 2_I, 2_H, 2_G(2), 2_F(2), 2_D(S),$
		$2_P, 2_S.$

Coupling of L and S also occurs, because both L and S if non-zero, generate magnetic field and thus tend to orient their moment with respect to each other in the direction where their interaction energy is least. This coupling is known as "LS coupling" and gives rise to the resultant angular momentum denoted by the quantum number J which may have quantized positive values from $(L + S)$ up to $(L - S)$ eg

in case of 3P ($L = 1$, $S = 1$) and 4F ($L = 3$, $S = 1\frac{1}{2}$) positive values of J representing states arising from term splitting are 2, 1 and 0 and $4\frac{1}{2}$, $2\frac{1}{2}$ and $1\frac{1}{2}$ respectively. Each state specified by J is $2J + 1$ fold degenerate. The total number of states obtained from a term is called multiplet and each value of J associated with a given value of L is called a component. Spectral transitions due to spin orbit coupling in atoms ion occurs between the components of two different multiplets. While LS coupling Scheme is used for the elements having atomic number less than 30, in whose case orbital interactions are relatively small, another scheme called "JJ coupling scheme" is used when spin orbital interactions are large and electron repulsion parameters decrease. The spin angular momentum of an individual electron couples with its orbital momentum to give an individual J for that electrons. The individual J 's couple to produce a resultant J for the atom. The electronic transitions taking place in an atom or ion are governed by certain "Selection Rules", which are as follows:

- i) Transition between states of different multiplicity are forbidden.
- ii) Transitions involving the excitation of more than one electron are forbidden.
- iii) In a molecule, which has a centre of symmetry,

transitions between two grade or two ungrade states are forbidden.

The ground term of a d^n system is the one which has the highest spin multiplicity and the highest L value. All the terms of a given system further split in the presence of a ligand field. Interelectronic repulsions within a configuration give the energies of the terms above the ground term. The energies are functions of two parameters related to the electronic repulsion. The two parameters may be chosen in either the way of condon and shortly (F_2 and F_4) or in that of Racah (B and C) for d orbital electrons. For the first transition series ions the value of C/B is around 4.0 and is about 1000 cm^{-1} . It is possible to examine the effects of crystal field on a Polyelectron configuration. The ligand field splitting due to cubic field can be obtained by considerations of group theory. It has been shown that an S state remains unchanged, P state does not split, a D state splits into two, F state into three and a G state into four states as tabulated below. This holds for an octahedral O_h as well as for T_d symmetry.

S	—————	A_1
P	—————	T_1
D	—————	$E + T_2$

$$\begin{array}{ll}
 F & \text{—————} \quad A_2 + T_1 + T_2 \\
 G & \text{—————} \quad A_1 + E + T_1 + T_2
 \end{array}$$

In weak crystal fields the inter electronic repulsions are larger. The crystal field may however, be of comparable magnitude (medium strength) or it may be larger than the inter electronic repulsion.

Correlation diagram for free ion (weak field): Strong-field configuration from d^1 to d^9 for both octahedral and tetrahedral cases are available. In addition to the qualitative aspects of transition from weak to strong crystal fields it is necessary to have quantitative results available for the interpretation of spectra. The so called Tanabe-Sugano diagrams make it possible. In these diagrams the energies of the levels of a d^n system as E/B are plotted as the vertical coordinate and the crystal field strength in the form of Dq/B as the horizontal coordinate. This diagram requires two parameters B and C for the interelectronic repulsions. It can be drawn only if the ratio C/B is specified.

Transition from the ground state to the excited state occurs according to selection rules described earlier. The energy level order of the state arising from the splitting

of a term state for a particular ion in an octahedral field is the reverse of that for this ion in a tetrahedral field.

Sometimes due to transfer of charge from ligand to metal or metal to ligand, bands appear in the ultraviolet region of the spectrum. Such spectra are known as "charge transfer spectra". For metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d-d transitions. However, these should be clearly discerned from the ligand bands which might also occur in the same region.

Magnetic Susceptibility:

The most rewarding application of magneto-chemistry has been one which deals with the coordination compounds. This is because the more important aspects of magneto-chemistry are concerned with the effect arising from the incomplete shells of electrons, isolated from each other and these conditions are fulfilled by the complex compounds of the transition metals.

There are several kinds of magnetism in substances viz., paramagnetism, diamagnetism and ferromagnetism or antiferromagnetism. The magnetic effects arising from the

spin angular momentum and orbital angular momentum of the electrons give rise to paramagnetism. Most of the compounds of the transition elements are paramagnetic. Diamagnetism is attributable to the closed shell electrons with an applied magnetic field. In the closed shell the electron spin moment and orbital moment of the individual electrons balance one another so that there is no magnetic moment. Ferromagnetism and antiferromagnetism arise as a result of interaction between dipoles of neighbouring atoms.

The magnetic properties of any individual atom or ion will result from some combination of these two properties, that is, the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus.

The spin value, i.e., the contribution to the moment from only the electron spin effect, is given by the equation:

$$\mu_s \text{ (in B.M)} = g\sqrt{S(S+1)}$$

where S is the spin quantum number and g is the gyromagnetic ratio or g factor and $\sqrt{S(S+1)}$ is the value of the angular momentum of the electron. Thus g is the ratio of

the magnetic moment to the angular momentum. μ_s is the spin magnetic moment of one electron in units of Bohr magnetons (1 B.M = $eh/4mc$).

When there is appreciable spin-orbit coupling in a molecule or ion which gives splitting of the ground state, that is, large compared to KT , $\lambda \gg KT$, where λ is the spin orbit coupling constant there will be an appreciable contribution to the moment from this coupling. The moment expected when spin orbit coupling is present is given by:

$$\mu_{s.o} = g \sqrt{J(J+1)} \quad \text{B.M}$$

where J is the total angular momentum of the ground state, given according to LS coupling, by $[L+S]$, $[L+S-1]$ --- $[L-S]$, if the shell is less than half filled with electrons, the ground state is $[L-S]$; and if it is more than half filled, it is $[L+S]$, for the gaseous atom, the g factor is given by the following formula:

$$g = \frac{1 + J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

The value for the measured magnetic moments close to the spin only value are expected for the spin free six coordinate complexes: t_2g^3 , $t_2g^3e_g^1$, $t_2g^6e_g^2$, $t_2g^6e_g^3$ and

for the spin paired complexes t_2g^6 , $t_2g^6eg^1$. For the first row transition metal ions in which quenching of the orbital contribution is expected to be complete, temperature independent paramagnetism accounts for the deviations of the measured moment, μ , from the spin only moment, μ_s . For those ions where spin-orbit coupling is appreciable the following equation shows the contribution of this effect to the measured moment

$$\mu = \mu_s \left[\frac{(1-\alpha)\lambda}{\Delta} \right]$$

where α is a constant for a metal ion, λ is the spin orbit coupling constant and Δ is the separation of the ground and excited states and can be obtained from the electronic spectra.

Generally the experimental effective magnetic moment of electron is higher than the spin magnetic moment of the electron. This is because the orbital motion of the electron also makes a contribution to the moment, if the orbital motion makes its full contribution to the magnetic moment then:

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

where L is the orbital angular momentum quantum of the ions.

While spin-magnetic moment is insensitive to environment of metal ion, the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and thereby an orbital magnetic moment with reference to a given axis it must be possible to transform the orbital into a fully equivalent orbital by rotation about that axis.

Electrons in dy states cannot contribute to the orbital moment because the $d_{x^2-y^2}$ and d_{z^2} orbitals cannot be transformed into one another by a rotation about any axis. However, all dE states excepting $d\epsilon^3$ and $d\epsilon^6$ contribute to the orbital moment.

No orbital contributions are expected for octahedral high spin complexes of configuration: $d^3(d\epsilon^3)$, $d^4(d\epsilon^3 dy)$, $d^5(d\epsilon^3 dy^2)$, $d^8(d\epsilon^6, dy^2)$, $d^9(d\epsilon^6 dy^3)$ while for $d^1(d\epsilon)$, $d^2(d\epsilon^2)$, $d^6(d\epsilon^4 dy^2)$ and $d^7(d\epsilon^5 dy^2)$ a non zero orbital moment contribution is possible. For low-spin complexes of octahedral symmetry and orbital moment contribution is seen for $d^4(d\epsilon^4)$ and $d^5(d\epsilon^5)$ and non for $d^6(d\epsilon^6)$ and $d^7(d\epsilon^6 dy)$.

In tetrahedral complexes due to term inversion it follows that where one does not expect orbital moment

contribution in O_h symmetry one expects it in T_d symmetry. For high-spin tetrahedral complexes no orbital moment contribution is, therefore, expected for dy^1 , dy^2 , $d \in^2$, $d \in^3$, $dy^3 d \in^3$, $dy^4 d \in^4$ while for $dy^2 d \in$, $dy^2 d \in^2$, $dy^2 d \in^4$, $dy^4 d \in^5$ no orbital moment is expected. Low spin tetrahedral complexes for central ion of first transition series are not generally known.

An orbital moment contribution is expected for tetrahedral and octahedral complexes when the ground state is split. However, the terms splitting into a three-fold orbitally degenerate state T will contribute but that splitting into a two-fold orbitally degenerate state E will not contribute as it is non-magnetic. The one-fold orbitally degenerate state A should give no orbital moment contribution.

Even when no splitting of the ground state appears in cases having no orbital moment contribution, an interaction with the higher states can appear due to spin-orbit coupling. giving an orbital moment transition metal series for the complexes, a decrease of the moment compared with the pure spin moment is expected, but in the second half of the series an increase should be seen. It has been found that for octahedral complexes there is appreciable orbital moment contribution and for tetrahedral complexes it is compara-

tively lesser.

The magnetic moments are not measured directly, therefore, one measures the magnetic susceptibility of a material from which it is possible to calculate the magnetic moment of the paramagnetic ion or atom.

If a substance is placed in a magnetic field of magnitude H , the flux B , with the substance is given by:

$$B = H + 4\pi I$$

where I is the intensity of magnetization. The ratio B/H is called the magnetic permeability of the material and is given by

$$B/H = 1 + 4\pi \left(\frac{I}{H}\right) = 1 + 4\pi K$$

where K is called the magnetic susceptibility per unit volume or volume susceptibility. B/H is the ratio of the density of lines of force within the substance to the density of such lines in the same region in the absence of the sample. Thus the volume susceptibility of a vacuum is by definition zero since in vacuum it must be $B/H = 1$.

Conventionally instead of volume susceptibility, gram susceptibility (χ_g) is used where magnetic suscepti-

bility is considered on weight basis. χ_g when multiplied by the molecular weight of the complex and corrected for diamagnetic values give rise to $\chi_M^{\text{Corr.}}$. The μ value is calculated from the $\chi_M^{\text{Corr.}}$ by the following expression:

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr.}} \cdot T} \quad \text{B.M.}$$

(2.52)

where 'T' is the absolute temperature at which the experiment is performed.

Magnetic susceptibility may or may not be dependent on the temperature as given by the Curie's law

$$\chi_M^{\text{corr}} = \frac{C}{T}$$

where 'T' is the absolute temperature and 'C' is a constant called Curie constant.

In general, however, deviations are found and μ_{eff} value depends on temperature within a certain limit of temperature range ($20^\circ - 40^\circ\text{K}$). The dependence of χ_M^{Corr} upon T is given by

$$\chi_M^{\text{corr}} = \frac{C}{T - \theta}$$

This equation expresses what is known as the Curie-Weiss

law and θ is called the Weiss constant.

In some systems the deviation from the Curie law is due to interionic or intermolecular interaction. As a result of these interactions the orientations of the magnetic dipoles are influenced by the orientation of the neighbours. In such condition the magnetic moment at a given temperature is given by:

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}} \cdot (T - \theta)}$$

Gouy magnetic balance is used for the measurement of magnetic susceptibility of the samples. In this method the sample was (finally) powdered and filled in the Gouy tube very carefully. The tube was suspended vertically between two poles of an electromagnet. The length of the tubes was adjusted in such a way that the lower end remained under the influence of the magnetic field. The weight of the tube containing sample was noted with the magnet on and off, the Gouy tube was calibrated with standard $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The gram susceptibility was calculated by the following formula:

$$\chi_g = \frac{\Delta H \ln K}{W \ln K} \cdot \frac{W_{\text{std}}}{\Delta W_{\text{std}}} \cdot \chi_{\text{std.}}$$

- χ_g = gram susceptibility of unknown sample
 $\Delta W_{\text{ln K}}$ = change in weight of unknown sample with magnet on and off.
 $W_{\text{ln K}}$ = weight of unknown sample.
 ΔW_{std} = change in weight of standard sample with magnet on and off.
 W_{std} = weight of the standard sample
 χ_{std} = gram susceptibility of the standard sample
 $\left[5.92 \times 10^{-6} \text{ for } \text{CuSO}_4 \right]$. unit? *252*
 ΔW = corrected = $\Delta W(\text{sample} + \text{tube}) - \Delta W(\text{empty tube})$.

Conductometry:

Electrolytic conductivity is a measure of the ability of a solution to carry electric current. Solution of electrolyte conduct an electric current by the migration of ions under the influence of an electric field. Like the metal conductor they obey Ohm's law. Thus if two platinum electrodes are inserted into a solution of electrolyte and connected to a source of electricity, then the current I flowing through the electrolyte will vary inversely with the resistance (R) and directly with the applied potential

difference (E) this may be expressed as

$$I = \frac{E}{R} \quad (1)$$

where I is the current in amperes, R is the resistance in ohms and E is the applied potential difference in volts. The term conductance is defined as the ease with which the current flows through the electrolytes. It can also be defined as the reciprocal of resistance.

$$C = \frac{I}{R} \quad (2)$$

The unit of conductance (C) is reciprocal ohm's or mhos.

The observed conductance C of a solution depends inversely on the distance l between two electrodes directly upon the area 'a', thus

$$C = K \frac{a}{l} \quad (3)$$

where 'K' is the specific conductance which is defined as the reciprocal of the resistance in ohm's of one cm. cube of liquid at a particular temperature. The unit of specific conductance is reciprocal ohm's or mhos.

The specific conductance is a suitable property for characterising metallic conductors, but it is not very good for electrolyte solution, because the specific conductance depends upon the concentration of solution as well, the electrical conductance of a solution depends upon the number of ions per unit volume of the solution and upon velocities with which these ions move under the influence of the applied electromotive force. As a solution of electrolyte is diluted, the specific conductance, K in equation (3) will decrease, since the number of ions available to carry an electric current in each cubic cm solution will also decrease.

In order to express the ability of individual ions to conduct, a function called the equivalent conductance is employed. It may be derived from equation (3) where (a) is the area of electrodes set one cm apart and are placed in an electrolyte solution containing one gm equivalent of the solute, if C_s is the concentration of the solution in gm equivalent per litre then the volume of the solution in cubic centimeter per equivalent is equal to $1000/C_s$, then equation (3) becomes

$$\Lambda = \frac{1000 K}{C_s} \quad (4)$$

where Λ is the equivalent conductance of the electrolyte.

Generally, the electrolytes behave on dilution in two ways:

- i) Electrolytes like NaOH and HCl have high value of conductivity even at low dilution and there is no rapid increase in their equivalent conductivity on dilution. Such electrolytes are called strong electrolyte. Mineral acids, alkali and alkaline earth hydroxides and most of other salts belong to this class.
- ii) Electrolytes like acetic acid have a low value of equivalent conductivity at higher concentration and there is a rapid increase in their equivalent conductivity on dilution. Such electrolytes are termed weak electrolytes. Most of the organic acids and bases belong to this class.

The solution whose conductivity is to be determined is placed in a special type of cell known as conductivity cell. There are various type of conductivity cells. The cell is made up of pyrex glass and the electrode contains

platinum disc coated with finely divided platinum black welded to platinum wires and fused in two glass tubes. The glass tubes contain mercury and are firmly fixed in the ebonite cover of the cell so that the distance between the electrodes may not change during the experiment. Since the conductance changes with temperature, it is necessary to keep the conductivity cell containing the solution in a thermostat.

Generally, the measured conductances are different from the specific conductance as the electrodes are not exactly 1 sq. cm. in area and 1 cm apart. Therefore, the conductance will have to be multiplied by a certain factor in order to get the correct value of specific conductances.

$$\text{specific conductance} = \frac{1}{a} \text{ conductance.}$$

The factor $1/a$ is known as cell constant the value of cell constant can be calculated from the following equation:

$$\text{Cell constant} = \frac{\text{specific conductance}}{\text{measured conductance}} \quad (5)$$

Once the cell constant has been determined, the molar conductance of an electrolyte solution can be easily obtained

by the following expression:

$$\Lambda_M = \frac{1000 \times \text{cell constant} \times \text{measured conductance}}{\text{concentration of solute expressed in mole cm}}$$

where Λ_M is the molar conductance of the solution.

Several studies of molar conductivities of different kinds of electrolytes in different solvents are now available^{82,83} and it is useful to compare Λ_M values of a given complex with that of the similar electrolyte. Conventionally solution of $10^{-3}M$ strength are used for the conductance measurement. Molar conductance value of different types of electrolytes in few solvents are given below:

A 1:1 electrolyte may have a value of $75-95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ in nitromethane, $50-75 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ in DMSO and $70-90 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ in DMF⁸²⁻⁸⁵.

CHAPTER - III

SYNTHESIS OF POTASSIUM DIHYDROBIS(1-INDAZOLYL) BORATE AND ITS COMPLEXES

SYNTHESIS OF POTASSIUM DIHYDROBIS (1-INDAZOLYL)BORATE AND
ITS COMPLEXES

EXPERIMENTALS

Analysis of carbon, hydrogen and nitrogen were done on a Coleman analyzer in microanalytical laboratory of the Chemistry Department, Aligarh Muslim University, Aligarh. For the metal estimation a known amount of complex was decomposed with a mixture of nitric-, perchloric- and sulphuric acids and the resulting solution were titrated against EDTA in presence of a PAN indicator. The halogen was estimated by fusing a known amount of the compound with fusion mixture (KNO_3 and K_2CO_3) and then precipitating the solution from AgNO_3 as AgX . The molar conductance of 10^{-3} M solution of the complexes were determined in nitrobenzene or dimethylformamide or indimethylsulfoxide using a Systronics conductivity bridge type 301-1 at room temperature.

The infrared and far infrared spectra were recorded in KBr and nujol respectively on a Perkin Elmer 521 (4000 - 650 cm^{-1}) and Beckman IR 12 ($650\text{-}250\text{ cm}^{-1}$).

Diffuse reflectance spectra were recorded on a Carl Zeiss VSU-2P Spectrophotometer using MgO as calibrant.

Magnetic susceptibility measurements were done at room temperature with a Gouy balance in the Chemistry Department of Guru Nanak Dev University, Amritsar.

The ligand, dihydrobis (1-indazolyl)borate anion, hydrotris (1-indazolyl)borate anion and tetrakis (1-indazolyl)borate anion were also characterized by their proton n.m.r. spectra on a varian A60D at Central Drug Research Institute, Lucknow.

Indazole (m.p. 147°C) was synthesized by a well known method, and was further purified by sublimation⁸⁶. Cu(II), Ni(II), Co(II), Mn(II), Fe(II), Zn(II), Cd(II) and Hg(II) chlorides (All B. D. H. Reagents) were recrystallized from

H_2O . (hydrolysis)

Synthesis of Potassium Dihydrobis (1-Indazoly1)Borate:

Potassium borohydride (1.0g) and indazole (8.7 g) were mixed together in a 1:4 molar ratio and heated in a flask to a temperature not exceeding 170° with constant stirring for 12 hours. The hydrogen evolved (2 moles) was collected over water. Toluene (300 cc) was then added to the resulting melt with vigorous stirring until it cooled to room temperature. The mixture was then filtered and the solid so obtained was washed twice with hot toluene and recrystallized from hexene m.p. 245°C yield : 52%.

Preparation of the complexes of dihydrobis(1-indazoly1)borate:

Chloro dihydrobis (1-indazoly1)borate copper(II), $\left[\text{Cu}(\text{C}_{14}\text{N}_4\text{BH}_{12})\text{Cl} \right] :$

An alcoholic solution of copper(II) chloride (1 gm) was slowly added to an appropriate saturated ligand solution. A green product was precipitated after standing the solution for few hours. It was filtered after twenty four hours and washed with alcohol and ether and dried in an oven at 180°C .

Chloro dihydrobis (1-indazoly1)borate nickel(II), $\left[\text{Ni}(\text{C}_{14}\text{N}_4\text{BH}_{12})\text{Cl} \right] :$

This murky yellow complex was also prepared in the manner described above by the addition of (1.21 gm) of ligand

with an appropriate metal chloride (1 gm) in ethyl alcohol. Here the solid appeared after a few hours in cold.

Chloro dihydrobis (1-indazoly1)borate cobalt (II),
 $[\text{Co}(\text{C}_{14}\text{N}_4\text{BH}_{12})\text{Cl}]$:

The buff coloured cobalt(II) complex of dihydrobis (1-indazoly1)borate was prepared by mixing an ethyl alcohol solution of the ligand (1.20 gm) with metal chloride (1 gm). The precipitate appeared after few hours, and was then filtered off, and dried at 180°C.

Chloro dihydrobis (1-indazoly1)borate manganese(II),
 $[\text{Mn}(\text{C}_{14}\text{N}_4\text{BH}_{12})\text{Cl}]$:

When a solution of manganese(II) chloride (1 gm) in 150 ml of ethyl alcohol was added to dihydrobis (1-indazoly1) borate (2.29 gm) in 100 ml of alcohol in an equimolar ratio, a white solid appeared after an hour. It was isolated, washed thoroughly with absolute alcohol and ether and then dried in an oven at 180°C.

Chloro dihydrobis (1-indazoly1)borate iron (III),
 $[\text{Fe}(\text{C}_{14}\text{N}_4\text{BH}_{12})\text{Cl}]$:

Addition of an alcoholic solution of potassium dihydrobis (1-indazoly1)borate to Fe(III) chloride in an

equimolar ratio yielded a greenish black solid. It was washed as usual and dried in an oven at 180°C.

Dihydrobis (1-indazolyl)borate zinc(II), $\left[\text{Zn}(\text{C}_{14}\text{N}_4\text{BH}_{12})_2 \right]$:

A solution of zinc(II) chloride (1 gm) in 50 ml of absolute alcohol was added to ligand (2.11 gm) in 100 ml of absolute alcohol, which after stirring for few hours gave a white solid. The complex was digested on a water bath for an hour and then filtered, washed with alcohol and dried in an oven at 100°C.

Dihydrobis (1-indazolyl)borate cadmium(II), $\left[\text{Cd}(\text{C}_{14}\text{N}_4\text{BH}_{12})_2 \right]$:

This complex was prepared by the procedure described for zinc(II) compound by adding alcoholic solution of cadmium chloride (1 gm) to the ligand (1.58 gm) alcoholic solution.

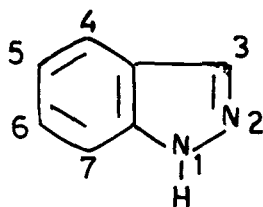
Dihydrobis (1-indazolyl)borate mercury(II), $\left[\text{Hg}(\text{C}_{14}\text{N}_4\text{BH}_{12})_2 \right]$:

When a solution of mercury(II) chloride (1 gm) in 50 ml of ethyl alcohol was added to dihydrobis (1-indazolyl)borate (1.06 gm) in 50 ml of alcohol, a white solid appeared after few days. It was isolated, washed with absolute alcohol and ether and then dried in an oven at 100°C.

Results and Discussion

The analytical results of the complexes, their colours and melting point, are given in table I. The experimental results are in agreement with the theoretical values. A general formula $M[H_2B(L)_2X]$ is suggested for all the complexes where $M = Cu(II), Ni(II), Co(II), Mn(II)$, $L =$ dihydrobis (1-indazolyl)borate and $X = Cl^-$. All the complexes are coloured except for manganese(II) complex, and stable at room temperature. Most complexes are generally insoluble in usual organic solvent except for a few which dissolve in nitrobenzen or dimethyl formamide or dimethyl sulfoxide.

Indazole has the following benzenoid structure (XII). It has two possible coordination sites viz., the pyridyl $\equiv N$ and pyrrole $>NH$ nitrogen atom in molecule.



Indazole
(XII)

In the formation of potassium dihydrobis(1-indazolyl) borate, the hydrogen atoms attached to nitrogen at position 1 in the two indazole molecules are removed, together with the two hydrogen atoms of potassium borohydride, releasing two moles of hydrogen. The ligand has been characterized by the appearance of a strong multiplet due to B-H stretch at 2420 and 2370 cm^{-1} and by the disappearance of N-H peak in the i.r. spectrum (Table - II). The characteristic frequencies of indazoles, reported earlier⁸⁷ also appear in this ligand. The $\nu(\text{C} = \text{N})$ band at 1500 cm^{-1} and the ring stretching frequency at 1620 cm^{-1} are similar to those observed in free indazole. The ligand was further characterized by its proton n.m.r. spectrum in DMSO which reveals a singlet at $\tau = 2.2$ assigned to the C-H proton peak of the pyrazole nucleus. The B-H proton peak was observed as a weakly resolved doublet at $\tau = 6.7$ ($J = 2.5$ Hz) and the aromatic proton peaks as a multiplet spread over the $J = 2.4$ -3.3, range, but clearly separated into the ortho and para ring protons.

The ligand was quite stable and remained unchanged even on heating to 100°C. On treatment with glacial acetic acid, the potassium salt yielded the free acid $\text{H}^+[\text{H}_2\text{B}(\text{InZ})_2]_2^-$ which was characterized by its elemental analysis and i.r. spectrum. The i.r. and n.m.r. spectra of the acid were

nearly similar to that of its parent compound. All the complexes had a 1:1 metal : ligand ratio. The result of the molar conductance measurements (Table - III) show that the Ni^{II} , Co^{II} , Mn^{II} , Fe^{III} complexes are ionic. The similarity between I. R. bands of free and chelated ligand is not surprising as there is little change in the frequencies of indazole after coordination with metal ions through the nitrogen atom at position 1 or 2 of the indazole ring system⁸⁷. Coordination is, therefore, proposed to occur through the nitrogen atom at position 1 as well as at position 2 in all the complexes. The BH_2 peak in the complexes is shifted positively by 20 - 100 cm^{-1} from its position in the free ligand. The M-N stretching frequency is in the 430-470 cm^{-1} range (Table - II).

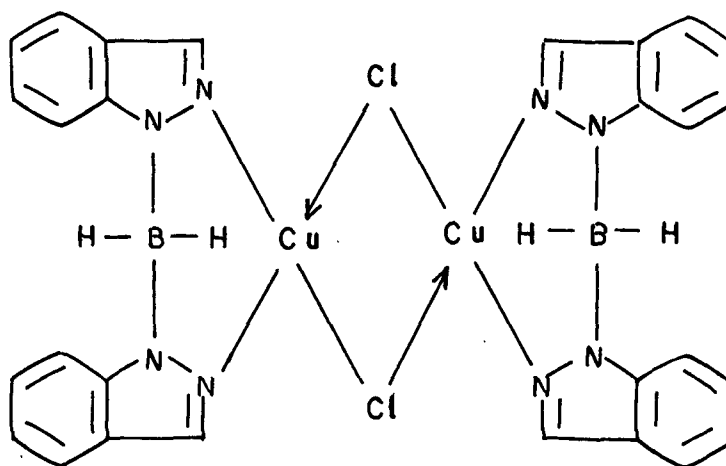
Electronic Spectra and Magnetic Susceptibilities:

The electronic spectra of the complexes are summarized in table III. The absorptions bands observed in 36,310 cm^{-1} to 37,000 cm^{-1} and 34,000 cm^{-1} to 34,500 cm^{-1} ranges in all the complexes are attributed to the ligand transition.

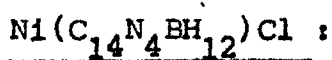
$\text{Cu}(\text{C}_{14}\text{N}_4\text{BH}_{12})\text{Cl}$:

The electronic spectrum of copper complex shows two main bands at 25,460 cm^{-1} and at 19,230 cm^{-1} , the latter of

$14,260\text{ cm}^{-1}$ and can be assigned to the crystal field transition of copper(II) ion, indicative of a distorted square planar configuration⁸⁸. The μ_{eff} value (1.51 B.M.) (Table-III) is however, lower than the normal value (1.9 B.M) which is probably due to antiferromagnetic interaction. A dimeric structure (XIII) is therefore proposed for this complex.

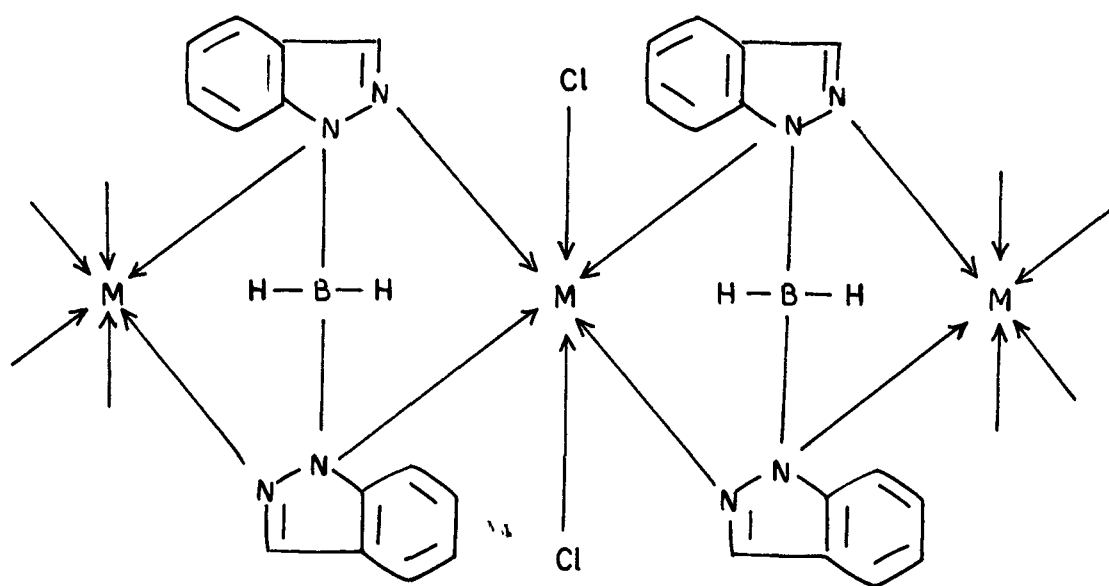


(XIII)

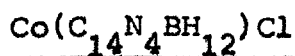


Its reflectance spectra shows absorptions at 8130 cm^{-1} , 14260 cm^{-1} and 22650 cm^{-1} assignable to ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$; ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ and ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ transitions respectively. This stoichiometric 1:1 nickel complex could

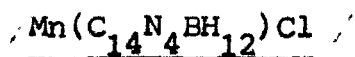
yield an octahedral structure (XIV) only through ligand bridging in a polymeric octahedral fashion, where each one nitrogen atom of the indazole ring system at position 2 and one nitrogen atom at position 1 is coordinated to one nickel ion, and another nitrogen atom at position 2 and nitrogen atom at position 1 to the adjacent nickel ion, thus completing the square plane. The other two positions of the octahedron are satisfied by coordination with a bridging chlorine above and below the plane. The lower μ_{eff} value (2.50 B.M) is also consistent with this geometry^{88,89}.



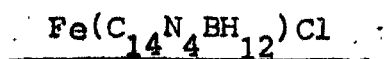
(XIV)



Even though the μ_{eff} value of 2.97 B.M. suggests a square planar geometry for cobalt complex, the electronic spectrum, in addition to a strong charge transfer band at $27,500 \text{ cm}^{-1}$ shows two absorption bands at 22670 cm^{-1} and $15,520 \text{ cm}^{-1}$ which could well be assigned to ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ transitions, respectively, for an octahedral Co(II) ion. Thus while the square planar structure may not completely be ruled out, it seems very likely that the cobalt complex has an octahedral structure. Such examples of anomalous magnetic moments for an octahedral Co(II) complexes are not uncommon⁹⁰⁻⁹².



The manganese complex may have an octahedral polymeric structure similar to that proposed for the nickel complex. The characteristic electronic spectra (Table - III) are consistent with the above geometry.



The iron ion in the complex is in +2 oxidation state. The low μ_{eff} value (5.06 B.M.) and the electronic spectrum suggests a dimeric octahedral geometry for this complex.

Potassium dihydrobis (1-indazolyl)borate zinc(II),
potassium dihydrobis (1-indazolyl)borate cadmium(II), and
potassium dihydrobis (1-indazolyl)borate mercury(II):

There is a negative shift in C = N stretching vibration in all the above complexes (except for Zn^{2+} , where there is a positive shift) indicating coordination through the nitrogen atom.

A comparison of the far IR spectra of the ligand and above complexes reveals that a new band, not present in the ligand, appears at 413, 422 and 420 cm^{-1} for the zinc, cadmium and mercury complexes respectively. These must presumably be due to the M - N stretching vibrations. All these complexes are diamagnetic.

In view of the limited studies, no definite assignment can be made about the geometry of the zinc, cadmium and mercury complexes.

TABLE - I
Analytical data, colour and melting points of potassium dihydrobis
(1-indazolyl)borate and its
complexes.

Complexes	Colour	M.p. ^o C	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Cl Found (Calcd)	% M Found (Calcd)
$(C_{14}N_4BH_{12})^+K^+$	White	245 ^o C	58.9 (58.5)	4.8 (4.1)	19.3 (19.9)	-	-
$Cu/C_{14}N_4BH_{12}/Cl$	Green	>360 ^o C	50.1 (48.5)	3.7 (3.4)	17.0 (16.1)	9.5 (10.1)	15.3 (14.8)
$Ni/C_{14}N_4BH_{12}/Cl$	Murky yellow	>360 ^o C	48.5 (49.1)	3.2 (3.5)	15.5 (16.3)	11.4 (10.5)	16.5 (17.2)
$Co/C_{14}N_4BH_{12}/Cl$	Buff	>360 ^o C	47.8 (48.9)	4.2 (3.4)	16.2 (16.0)	9.6 (10.5)	18.0 (17.2)
$Mn/C_{14}N_4BH_{12}/Cl$	White	>360 ^o C	48.6 (49.8)	3.7 (3.5)	15.5 (16.6)	10.9 (10.5)	16.8 (16.3)
$Fe/C_{14}N_4BH_{12}/Cl$	Greenish black	>360 ^o C	49.1 (49.7)	3.7 (3.5)	16.1 (16.5)	10.5 (10.6)	15.8 (16.2)
$Zn/C_{14}N_4BH_{12}/Cl$	Light pink	210 ^o C	59.8 (60.0)	4.2 (3.2)	19.4 (20.3)	-	11.2 (11.6)
$Cd/C_{14}N_4BH_{12}/Cl$	Dirty white	310 ^d	53.6 (55.4)	3.8 (3.9)	17.9 (18.4)	-	19.2 (18.4)
$Hg/C_{14}N_4BH_{12}/Cl$	Grey	>360 ^o	48.8 (48.3)	3.2 (3.4)	15.5 (16.1)	-	27.9 (28.7)

d = decomposition temperature

TABLE - II
I.R. Spectra of potassium dihydrobis(1-indazolyl)borate and its
complexes.

Compound	ν B - H	Ring stretching	ν C = N	ν M - N	ν M - Cl
$(C_{14}N_4BH_{12})^{-}K^{+}$	2420 m, sh 2370 w	1620 s	1500 s	-	-
Cu $\nearrow C_{14}N_4BH_{12} \nearrow Cl$	2466 m, sh 2350 sh	1620 s	1510 s	430 s	305 s
Ni $\nearrow C_{14}N_4BH_{12} \nearrow Cl$	2466 m, sh 2350 sh	1620 s	1510 s	430 s	325 s
Co $\nearrow C_{14}N_4BH_{12} \nearrow Cl$	2420 m 2520 m	1625 s	1510 s	470 s	355 w
Mn $\nearrow C_{14}N_4BH_{12} \nearrow Cl$	2320 m, sh 2340 m	1620 s	1510 s	455 s	360 s
Fe $\nearrow C_{14}N_4BH_{12} \nearrow Cl$	2320 m, sh 2350 w	1615 s	1510 s	470 s	340 s
Zn $\nearrow C_{14}N_4BH_{12} \nearrow 2$	2335 m, sh 2360 w	1640 w 1670 w	1452 s	413 s	380 s
Cd $\nearrow C_{14}N_4BH_{12} \nearrow 2$	2320 m 2340 m, sh	1622 s	1453 s	422 s	385 s
Hg $\nearrow C_{14}N_4BH_{12} \nearrow 2$	2325 m 2345 m, sh	1610 s	1450 s	420 s	380 s

TABLE - III

Molar conductance (Λ_M) values ($\text{ohm}^{-1} \text{cm}^2$), electronic spectra and μ_{eff} values of complexes of potassium dihydrobis(1-indazolyl)borate					
Complexes	μ_{eff} B.M.	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance	
				DMSO	DMF Nitrobenzene
$\text{Cu}[\text{C}_{14}\text{N}_4\text{BH}_{12}]/\text{Cl}$	1.51	36,310 34,430 25,640 19,230 14,260			1.62
$\text{Ni}[\text{C}_{14}\text{N}_4\text{BH}_{12}]/\text{Cl}$	2.50	36,980 34,430 26,650 14,260 8,130	$3T_1(P) \leftarrow$ $3T_1g(F) \leftarrow$ $3T_1g(F) \leftarrow$ $2g$ $3A_2g(F)$ $3A_2g(F)$ $3A_2g(F)$	-	106.4 -
$\text{Co}[\text{C}_{14}\text{N}_4\text{BH}_{12}]/\text{Cl}$	2.97	36,970 34,330 27,550 22,670 15,520	$4T_1(P) \leftarrow$ $4T_1g(F) \leftarrow$ $4A_2g$ $4T_1g(F)$ $4T_1g(F)$ $1g$		89.6
$\text{Mn}[\text{C}_{14}\text{N}_4\text{BH}_{12}]/\text{Cl}$	Paramagnetic	36,970 34,350 25,160 24,750 18,650	$4T_1(G) \leftarrow$ $4E_1g(G) \leftarrow$ $4T_1g(F) \leftarrow$ $1g$ $6A_1g$ $6A_1g$ $6A_1g$	43.7	

..... contd

TABLE - III: contd

Complexes	μ_{eff} B.M.	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance	
				DMSO	DMF Nitrobenzene
$\text{Fe} / \text{C}_{14}\text{N}_4\text{BH}_{12} / \text{Cl}$	5.06	36,330	$5E_g \leftarrow 5T_{2g}$	-	48.5
		34,410			
		20,850			
		14,840			
		11,200			
$\text{Zn} / \text{C}_{14}\text{N}_4\text{BH}_{12} / 2$	Diamag- netic	-	-	68.4	-
$\text{Cd} / \text{C}_{14}\text{N}_4\text{BH}_{12} / 2$	Diamag- netic	-	-	-	53.2
$\text{Hg} / \text{C}_{14}\text{N}_4\text{BH}_{12} / 2$	Diamag- netic	-	-	69.5	-

CHAPTER - IV

SYNTHESIS OF POTASSIUM HYDROTRIS(1-INDAZOLYL) BORATE AND ITS COMPLEXES

SYNTHESIS OF POTASSIUM HYDROTRIS(1-INDAZOLYL) BORATE AND ITS COMPLEXES

Synthesis of Potassium Hydrotris (1-Indazolyl) Borate

Potassium borohydride (1.0 g) and indazole (6.55 gm) were mixed together and heated up to 200°C with constant stirring in a sealed flask for twelve hours. The hydrogen gas corresponding to three equivalent was collected over water. Now 300 ml of the toluene was added to the resulting melt which was stirred until the contents cooled down to room temperature. It was then filtered and the solid thus obtained was washed twice with hot toluene and recrystallized from hexene, m.p. 230-232°C. yield 50%.

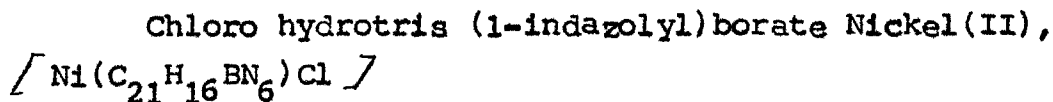
Preparation of Potassium Hydrotris (1-Indazolyl) borate Complexes

Chloro hydrotris (1-indazolyl) borate copper(II),

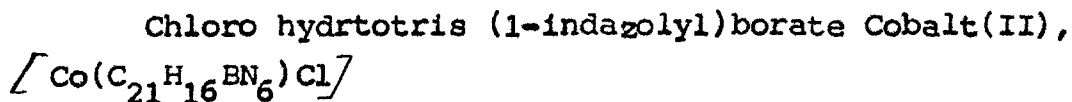
$$\left[\text{Cu}(\text{C}_{21}\text{H}_{16}\text{BN}_6)\text{Cl} \right]$$

A solution of 1 gm of copper chloride in 200 ml of absolute alcohol was added to 1.67 gm of the ligand in 100 ml of absolute alcohol, which, after stirring for few hours gave a light green solid. The complex was digested on a water bath for an hour and then filtered and washed with

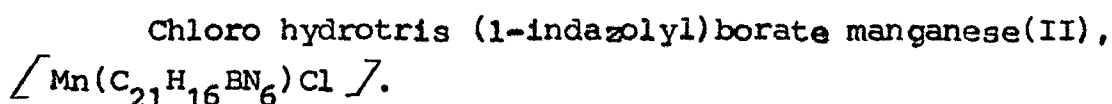
alcohol, ether and dried in an oven at 100°C.



This complex was prepared by the procedure described above for Cu(II) compound by adding alcoholic solution of nickel chloride to the ligand (alcoholic) solution.



An alcoholic solution of the ligand (1.68 gm) was mixed with an alcoholic solution of cobalt chloride (1 gm) in equimolar ratio and refluxed for two and a half hours. It yielded a buff coloured solid. It was isolated and dried in the usual manner.



This white solid was prepared by a method as described for nickel complex. An alcoholic solution of manganese chloride (1 gm) was added to the ligand solution (3.2 gm) in equimolar ratio in the same solvent. A solid appeared after keeping this for few hours. The solid thus obtained was filtered, washed with ethanol and dried at 150°C.

Chloro hydrotris (1-indazoly1)borate Iron(II),
 $[\text{Fe}(\text{C}_{21}\text{H}_{16}\text{BN}_6)\text{Cl}]$.

This complex was synthesized by mixing the alcoholic solutions of the ligand and the salt in equimolar ratio. The complex was isolated and purified in the same manner as described earlier. Immediate precipitation occurred on mixing the two solutions. The solid thus obtained was digested on a water bath, filtered, washed several times with alcohol and ether and dried in vacuum at 100°C . The wine red coloured solid was insoluble in usual organic solvents.

Hydrotris(1-indazoly1)borate Zinc(II),
 $\text{Zn}(\text{C}_{21}\text{H}_{16}\text{BN}_6)_2$.

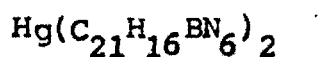
The white coloured zinc complex of hydrotris (1-indazoly1)borate was prepared by mixing an ethyl alcohol solution of the ligand (2.9 gm) with zinc chloride (1 gm). The precipitate appeared after few hours and was filtered off, and dried at 150°C .

Hydrotris (1-indazoly1)borate cadmium(II),
 $\text{Cd}(\text{C}_{21}\text{H}_{16}\text{BN}_6)_2$.

Addition of an alcoholic solution of potassium hydrotris (1-indazoly1)borate to cadmium(II) chloride in an equi-

molar ratio yielded a white solid. It was washed as usual and dried in an oven at 150°C.

Hydrotris(1-indazolyl)borate mercury(II),



This white solid was prepared by a method as described for zinc complex. An alcoholic solution of mercury(II) chloride (1.0 gm) was added to the ligand solution (1.48 gm) in the same solvent. A solid appeared after keeping this for few hours. The solid thus obtained was filtered, washed with ethanol and dried at 150°C.

Results and Discussion

The analytical results, colour and melting points of the complexes are given in table-IV. The experimental results are in good agreement with the proposed composition of the complexes. All the complexes are of the type $M[\text{HB}(\text{L})_3]_2$, where L = potassium hydrotris (1-indazolyl) borate; X = Cl^- ; M = Cu(II), Ni(II), Co(II), Mn(II), Fe(III), Zn(II), Cd(II) and Hg(II). These complexes are stable at room temperature.

When potassium borohydride and indazole were mixed together under molten condition, evolution of hydrogen took place. At 200°C , three equivalents of hydrogen was removed and potassium hydrotris (1-indazolyl)borate melting at $230\text{--}232^\circ\text{C}$ was obtained. The authenticity of this ligand has been verified by the appearance of a $\nu(\text{B-H})$ and $\nu(\text{B-N})$ peak^{93,94} at 2410 cm^{-1} at 1113 cm^{-1} respectively and also by the disappearance of the $\nu(\text{N-H})$ peak in its I.R. spectrum. The $\nu(\text{C}=\text{N})$ appears at 1490 cm^{-1} which is not much different from that observed in free indazole⁸⁷. It was further characterized by its proton n.m.r. spectrum in dimethyl sulfoxide which reveals a singlet at $\tau = 2.1$ assigned to C - H proton peak of the pyrazole nucleus. The B - H proton peak was observed at $\tau = 6.3$. The aromatic proton

peaks were observed in the form of two multiplets spread over $J = 2.4$ to 2.8 $J = 2.9$ to 3.4 .

The complexes were formed in a 1:1 metal : ligand ratio. They were all high melting solids (Table-IV). They were soluble either in dimethyl formamide or dimethyl sulfoxide or nitrobenzene. The molar conductance values of 10^{-3} solution of complexes in the above solvents indicate a nonionic nature except for the nickel complex.

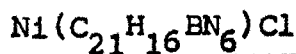
The I.R. spectra of the complexes revealed no marked shift in the $C = N$ and the ring frequencies of the ligand. Coordination is, therefore, proposed to occur through the pyridyl nitrogen as well as through the pyrrole nitrogen atom. In all the cases a new band in $420-480\text{ cm}^{-1}$ range has been assigned to the $M - N$ stretching frequency. These complexes appear to have a structure similar to dihydrobis(1-indazolyl) borate complexes reported earlier⁹⁵.

Electronic Spectra and Magnetic Susceptibilities

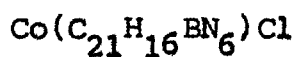
Since the bands in the range $36,720\text{ cm}^{-1}$ to $36,760\text{ cm}^{-1}$ and $36,750\text{ cm}^{-1}$ have been observed in all the complexes they have been assigned to the ligand transitions (Table-VI).



The copper complex shows two main bands at $24,530\text{ cm}^{-1}$ and $19,330\text{ cm}^{-1}$ along with a shoulder at $14,260\text{ cm}^{-1}$ and can be assigned to crystal field transition of copper(II) ion, indicative of a distorted square planar geometry⁹¹. The μ_{eff} value of 1.85 B.M. for this complex also supports the proposed configuration.

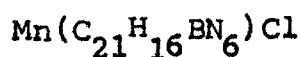


There are three bands in the nickel complex at $8,280\text{ cm}^{-1}$, $14,320\text{ cm}^{-1}$ and $20,200\text{ cm}^{-1}$ assignable to ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{T}_{2g}(\text{F})$ and ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{T}_{2g}(\text{F})$ transition for an octahedral geometry. However, the μ_{eff} value is lower (Table-VI) than that expected for an octahedral Ni(II) ion. It is therefore, suggested that the nickel has a dimeric octahedral geometry involving halogen bridging.

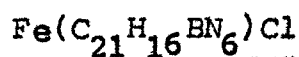


Besides a charge transfer band at $27,240\text{ cm}^{-1}$ in $\text{Co}[\text{HB}(\text{InZ})_3]\text{Cl}$, there are two more bands (Table-VI) consistent with an octahedral geometry for cobalt(II) ion though the μ_{eff} value is not in consonance with the proposed geometry. Such an anomalous magnetic moment for an octahedral

Co(II) complex in several other cases have also been encountered^{91,92}.



The manganese complex may also have an octahedral dimeric structure similar to that proposed for the nickel complex.



In the electronic spectrum of this complex the bands at 20,340 and 15,170 cm^{-1} must be attributed to charge transfer. While only one band at around 11,130 cm^{-1} should be expected for the ${}^5\text{E}_g \longleftarrow {}^5\text{T}_{2g}$ transition in this case having an octahedral geometry. The very weak bands observed at 11,000, 10,600 cm^{-1} must be due to the splitting of ${}^5\text{E}_g$ level because of the Jahn-Teller effect⁹⁶.

The μ_{eff} value of 5.20 B.M for iron complex and its electronic spectrum (Table-VI) suggests a dimeric octahedral geometry.

Ptassium hydrotris (1-indazolyl)borate zinc(II), potassium hydrotris(1-indazolyl)borate cadmium(II) and potassium hydrotris (1-indazolyl)borate mercury(II).

In all the above complexes (except for Cd^{2+} , where there is positive shift) there is a negative shift in C = N stretching vibration indicating coordination through the nitrogen atom.

A comparison of the far I.R. spectra of the ligand and above complexes reveals that a new band, not present in the ligand, appears at 1452, 1,500 and 1,450 cm^{-1} for the zinc, cadmium and mercury complexes respectively. There must presumably be due to the M-N stretching vibration. All the complexes are diamagnetic.

In view of the limited studies no definite assignment can be made about the geometry of the zinc, cadmium and mercury complexes.

TABLE - IV

Analytical data, colour and melting points of potassium hydrotris(1-indazolyl) borate and its complexes

Complexes	Colour	M.p. ^o C	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Cl Found (Calcd)	% M Found (Calcd)
$(C_{21}N_6BH_{16})^{-}K^{+}$	White	230 ^o C	63.0 (62.5)	3.9 (3.9)	20.2 (20.8)	-	-
$Cu[C_{21}N_6BH_{16}]Cl$	Light green	>360 ^o C	53.8 (54.5)	3.8 (3.40)	18.0 (18.1)	8.4 (7.5)	13.6 (13.6)
$Ni[C_{21}N_6BH_{16}]Cl$	Pinkish yellow	335-336d	56.0 (55.1)	3.3 (3.5)	18.8 (18.3)	6.8 (7.6)	12.9 (12.6)
$Co[C_{21}N_6BH_{16}]Cl$	Buff	>360 ^o C	54.3 (55.0)	3.8 (3.4)	19.1 (18.3)	7.2 (7.6)	11.9 (12.8)
$Mn[C_{21}N_6BH_{16}]Cl$	White	356-357d	54.8 (55.6)	3.9 (3.5)	19.3 (18.5)	6.9 (7.72)	12.5 (12.1)
$Fe[C_{21}N_6BH_{16}]Cl$	Wine red	>360 ^o C	54.8 (55.5)	3.2 (3.5)	17.6 (18.5)	7.5 (7.8)	12.8 (12.3)
$Zn[C_{21}N_6BH_{16}]_2$	White	>360 ^o C	64.2 (64.6)	3.8 (4.1)	20.8 (21.5)	-	9.1 (8.3)
$Cd[C_{21}N_6BH_{16}]_2$	White	>360 ^o C	60.5 (60.9)	4.2 (3.8)	20.1 (20.3)	-	13.4 (13.5)
$Hg[C_{21}N_6BH_{16}]_2$	Grey	>360 ^o C	54.3 (55.0)	4.1 (3.5)	17.5 (18.3)	-	21.8 (21.8)

d = decomposition temperature

TABLE - V

I.R. Spectra of potassium hydrotris(1-indazolyl)borate and its complexes

Compound	ν B - H (cm^{-1})	Ring stretching (cm^{-1})	ν C = N (cm^{-1})	ν M - N (cm^{-1})	ν M - Cl (cm^{-1})
$(\text{C}_{21}\text{N}_6\text{BH}_{16})^-\text{K}^+$	2410 b	1610 s	1490 s	-	-
$\text{Cu}/\text{C}_{21}\text{N}_6\text{BH}_{16}/\text{Cl}$	2340 sh	1610 s	1480 s	425 s	295 w
$\text{Ni}/\text{C}_{21}\text{N}_6\text{BH}_{16}/\text{Cl}$	2460 m, sh	1615 s	1495 s	430 s	315 s
$\text{Co}/\text{C}_{21}\text{N}_6\text{BH}_{16}/\text{Cl}$	2340 m	1620 s	1503 m	435 s	292 s
$\text{Mn}/\text{C}_{21}\text{N}_6\text{BH}_{16}/\text{Cl}$	2348 m	1615 s	1500 s	480 m	295 s
$\text{Fe}/\text{C}_{21}\text{N}_6\text{BH}_{16}/\text{Cl}$	2335 b	1610 s	1485 w	450 s	305 s
$\text{Zn}/\text{C}_{21}\text{N}_6\text{BH}_{16}/\text{Cl}$	2345 b	1665 w	1452 s	413 s	305 s
$\text{Cd}/\text{C}_{21}\text{N}_6\text{BH}_{16}/\text{Cl}$	2330 b	1622 s	1453 s	422 s	310 s
$\text{Hg}/\text{C}_{21}\text{N}_6\text{BH}_{16}/\text{Cl}$	2330 b	1610 s	1450 s	421 w	300 s

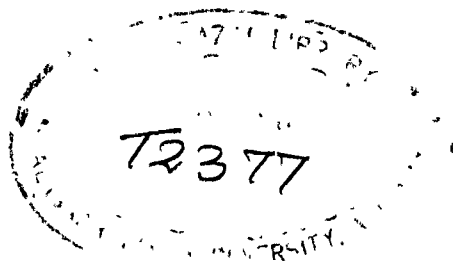


TABLE - VI

Molar conductance (Λ_M) values ($\text{ohm}^{-1} \text{cm}^2$), electronic spectra and μ_{eff} values of complexes of potassium hydrotris(1-indazolyl)borate.

Compounds	μ_{eff} B.M.	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance	
				DMSO	DMF Nitrobenzene
$\text{Cu}[\text{C}_{21}\text{N}_6\text{BH}_{16}]/\text{Cl}$	1.85	36,760			
		33,430			
		24,530		-	1.86
		19,330			
		14,260			
$\text{Ni}[\text{C}_{21}\text{N}_6\text{BH}_{16}]/\text{Cl}$	2.82	36,760			
		34,220			
		26,650			
		20,200			
		14,320			
		8,280			
			$3T_1(P) \leftarrow 3A_1(F)$ $3T_1g(F) \leftarrow 3A_2g(F)$ $3T_1g(F) \leftarrow 3A_2g(F)$ $2g$	-	123.2
$\text{Co}[\text{C}_{21}\text{N}_6\text{BH}_{16}]/\text{Cl}$	2.87	36,720			
		33,450			
		27,240			
		21,680			
		15,240			
			$4T_1(P) \leftarrow 4T_1(F)$ $4A_1g(F) \leftarrow 4T_1g(F)$ $1g$	-	4.7
$\text{Mn}[\text{C}_{21}\text{N}_6\text{BH}_{16}]/\text{Cl}$	Paramagnetic	36,650			
		33,280			
		25,270			
		24,520			
		18,640			
			$4A_1(G) \leftarrow 6A_1g$ $4E_1g(G) \leftarrow 6A_1g$ $4T_1g(F) \leftarrow 6A_1g$ $1g$	42.5	-

.....contd.....

TABLE - VI: contd

Compounds	μ_{eff} B.M.	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance		
				DMSO	DMF	Nitrobenzene
$\text{Fe} \left[\text{C}_{21}\text{N}_6\text{BH}_{16} \right] \text{Cl}$	5.20	$\left. \begin{array}{l} 36,650 \\ 33,440 \\ 20,340 \\ 15,170 \\ 11,130 \end{array} \right\}$	$\left. \begin{array}{l} ? \\ 5E_g \end{array} \right\} \xrightarrow{\quad} 5T_{2g}$	-	43.6	-
$\text{Zn} \left[\text{C}_{21}\text{N}_6\text{BH}_{16} \right]_2$	Diamag- netic	-	-	64.8	-	-
$\text{Cd} \left[\text{C}_{21}\text{N}_6\text{BH}_{16} \right]_2$	Diamag- netic	-	-	68.8	-	-
$\text{Hg} \left[\text{C}_{21}\text{N}_6\text{BH}_{16} \right]_2$	Diamag- netic	-	-	-	55.6	-

CHAPTER - V

SYNTHESIS OF POTASSIUM TETRAKIS (1-INDAZOLYL) BORATE AND ITS COMPLEXES

SYNTHESIS OF POTASSIUM TETRAKIS (1-INDAZOLYL) BORATE AND ITS COMPLEXES

Synthesis of Potassium Tetrakis (1-Indazolyl) Borate

Potassium borohydride (1.0 g) and indazole (8.7 g) were heated together in a flask in an oil bath in a sealed system up to 215°C until about 415 ml of hydrogen was evolved. When the contents of the flask came under sufficiently molten condition to allow free movement of the magnetic stirrer. This melt was stirred thoroughly till it became viscous. When the hydrogen gas ceased to evolve, the contents were cooled to room temperature. It was then poured into 250 ml of toluene. This mixture was filtered and washed with hot toluene to remove traces of indazole and recrystallised from a hexene-ethanol mixture. It was dried at 150°C., m.p. 220°C yield : 48%.

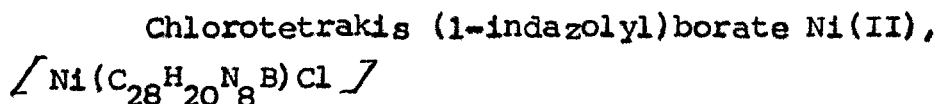
Preparation of the Complexes:

Chlorotetrakis (1-indazolyl) borate Cu(II),

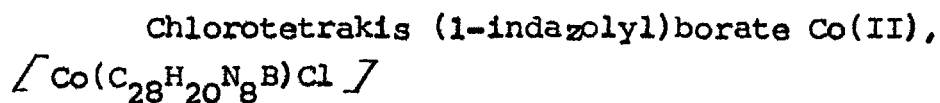
$$\left[\text{Cu}(\text{C}_{28}\text{H}_{20}\text{N}_8\text{B})\text{Cl} \right]$$

An alcoholic solution of 0.34 g of copper(II) chloride was added to the ligand solution (1.04 gm) in an equimolar ratio, which yielded a green solid immediately. It was

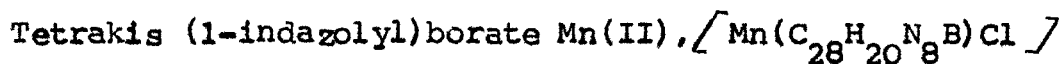
digested on a water bath for an hour and filtered, washed thoroughly with absolute alcohol, ether and dried in an oven.



This light pink complex was prepared by the same procedure as described for the above complex, adding an ethanolic solution of the metal chloride (0.47 g) to the ligand solution (1.04 g). It was isolated and dried in the manner described above.



An alcoholic solution of the ligand was added to metal chloride dissolved in the same solvent in a 1:1 metal to ligand ratio. It was refluxed for 2-3 hours. The buff fluffy complex so formed was isolated in the same way as described earlier.



The ligand (1.94 g) was added to an alcoholic solution of the manganese chloride (0.39 g) in equimolar ratio. The solid thus obtained was filtered, washed with ethanol and dried at 150°C.

Tetrakis(1-indazolyl)borate Fe(II), $\left[\text{Fe}(\text{C}_{28}\text{H}_{20}\text{N}_8\text{B})\text{Cl} \right]$

An alcoholic solution of iron chloride (0.39 g) was added to an alcoholic solution of potassium tetrakis (1-indazolyl)borate (1.04 g) in an equimolar ratio. After few minutes a red coloured solid appeared which was isolated and dried as usual.

Results and Discussion

The composition of potassium tetrakis(1-indazolyl) borate was established by elemental analysis and by the disappearance of the $\nu(\text{B-H})$ band at 2410 cm^{-1} confirming that all the hydrogen atoms have been replaced. It was further characterized by the disappearance of the $\nu(\text{N-H})$ peak at 3450 cm^{-1} from the ligand. The other frequencies of indazole in potassium dihydrobis(1-indazolyl)borate reported in the preceding chapter also appear in potassium tetrakis (1-indazolyl)borate. The $\nu(\text{C}=\text{N})$ and the ring stretching frequencies appearing at 1485 cm^{-1} and 1600 cm^{-1} , respectively, are not much different from that of the free indazole and potassium dihydrobis(1-indazolyl)borate^{87,95}. The boron in potassium tetrakis (1-indazolyl)borate is bound to four indazolyl groups through the nitrogen atom at position 1 and each indazolyl moiety contains two nitrogen atoms which can act as coordination sites for metal ions.

The complexes synthesized, have a 1:1 metal:ligand ratio (Table-VII). They are thermally stable and insensitive to air. The change in the I.R. spectrum on going from free to complexed ligand is unusual. The ligand ring frequencies at 1600 and 1495 cm^{-1} shift to higher frequencies on complexation (Table-VIII) and are similar to the shifts observed in

in the complexes of boron trichloride with pyridine and piperidine⁹⁴. The M - N stretching frequency lies in the 380-430 cm^{-1} range (Table-VIII). The molar conductance values of 10^{-3}M solutions of all complexes except for the Ni(II) complex, in different solvents support a nonionic species (Table-IX) which may be due to the polar nature of the solvent⁹⁷.

Electronic Spectra and Magnetic Susceptibilities

The electronic spectra of the metal complexes of tetrakis (1-indazolyl)borate have been summarized in table-IX. Since the bands observed in the range 36,560 to 36,520 cm^{-1} and 34,440 to 34,210 cm^{-1} appear in all the complexes (Table-IX) they are attributed to ligand transitions.

In the case of tetrakis(1-pyrazolyl)borate complexes with divalent metal halides all the halogens have been replaced by the ligand giving a 1:2 complex⁹⁸, but in the present cases only one halogen is replaced. It also implies that the coordination behaviour of tetrakis (1-indazolyl) borates is different from that of the above ligand.

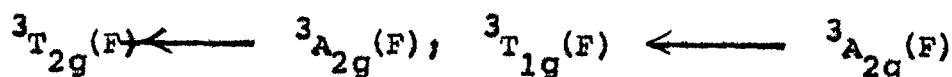
$[\text{Cu B(InZ)}_4\text{Cl}]$

The electronic spectrum of $\text{CuB(InZ)}_4\text{Cl}$ shows a strong band at 19,210 cm^{-1} along with a shoulder at 13,920 cm^{-1}

(Table-IX) which may be assigned to ${}^2A_{1g} \longleftarrow {}^2B_{1g}$ and ${}^2E_g \longleftarrow {}^2B_{1g}$ transitions respectively, of Cu(II) ion in a distorted square planar configuration (Fig. XV). The μ_{eff} value of 1.88 B.M (Table-IX) is also consistent with the accepted value of square planar Cu(II) complexes⁸⁸.

$[NiB(InZ)_4Cl]$

The nickel complex shows three bands at $8,330\text{ cm}^{-1}$, $14,520\text{ cm}^{-1}$ and $21,600\text{ cm}^{-1}$ assignable to

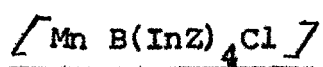


and ${}^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$ transitions for an octahedral nickel ion⁹⁸. The μ_{eff} value of 2.87 B.M of Ni(II) in $NiB(InZ)_4Cl$ is slightly lower than that expected for an octahedral geometry, which is probably due to ligand bridging.

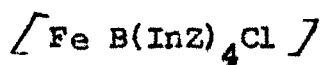
$[CoB(InZ)_4Cl]$

There is a strong charge transfer band at $27,240\text{ cm}^{-1}$ in $CoB(InZ)_4Cl$. The other bands (Table-IX) at $21,540\text{ cm}^{-1}$ and $15,260\text{ cm}^{-1}$ assigned to ${}^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \longleftarrow {}^4T_{1g}(F)$ transitions respectively, are suggestive of an octahedral geometry for Co(II)^{91,92}. However, the μ_{eff} value (2.93 B.M) for Co(II) in $Co[B(InZ)_4]Cl$ is

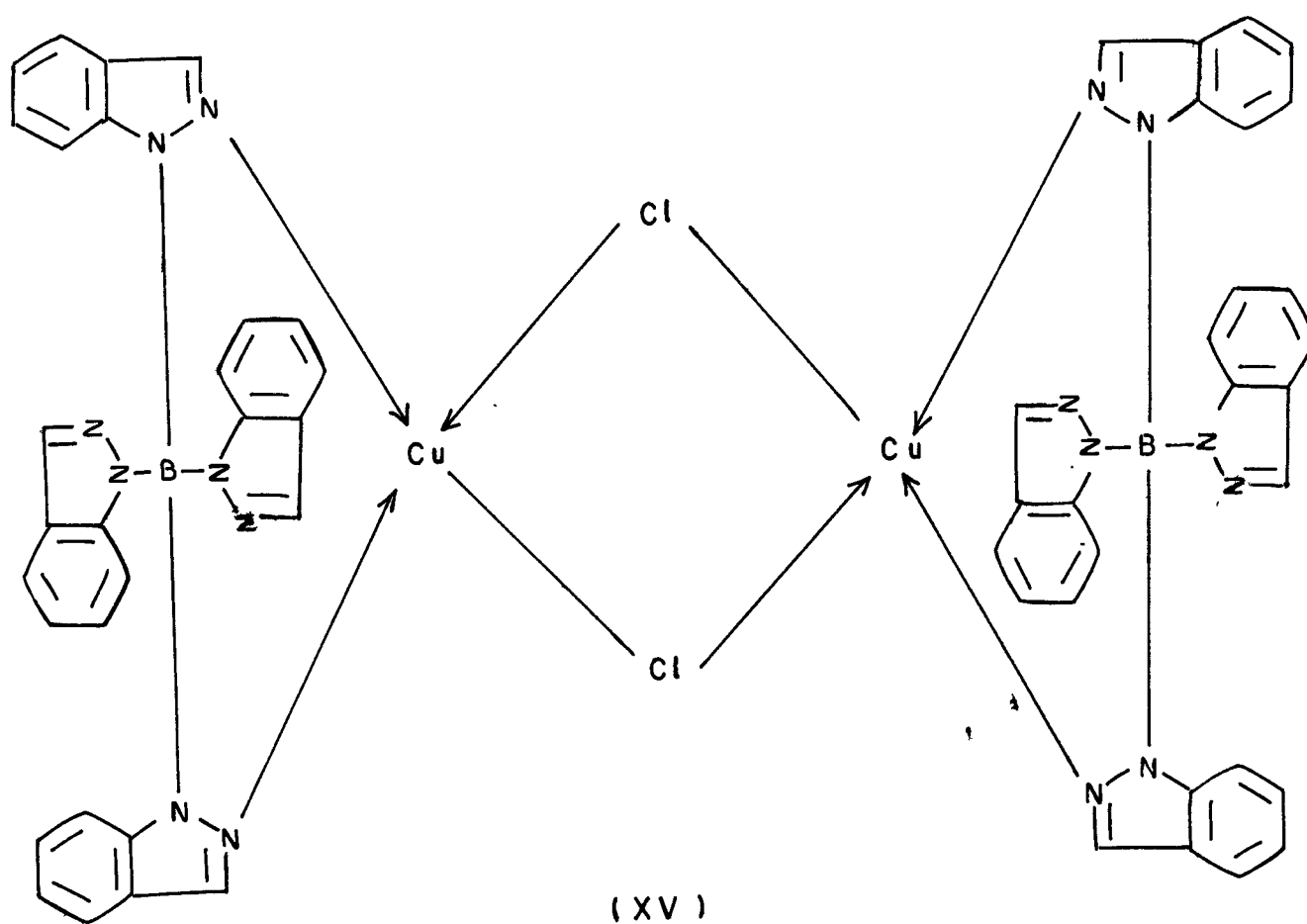
lower for an octahedral Co(II) complex in high spin state (4.8-5.6 B.M) but it is higher in low spin state (1.73-2.0 B.M). Such an anomalous intermediate μ_{eff} value is not uncommon for Co(II) complexes with an octahedral geometry (Fig. XVI).



The electronic spectral bands for the manganese(II) complex (Table-IX) are consistent with an octahedral geometry.



The μ_{eff} value of 5.28 B.M for iron(II) complex as well as its electronic spectrum are consistent with an octahedral geometry about a high spin Fe(III) core.



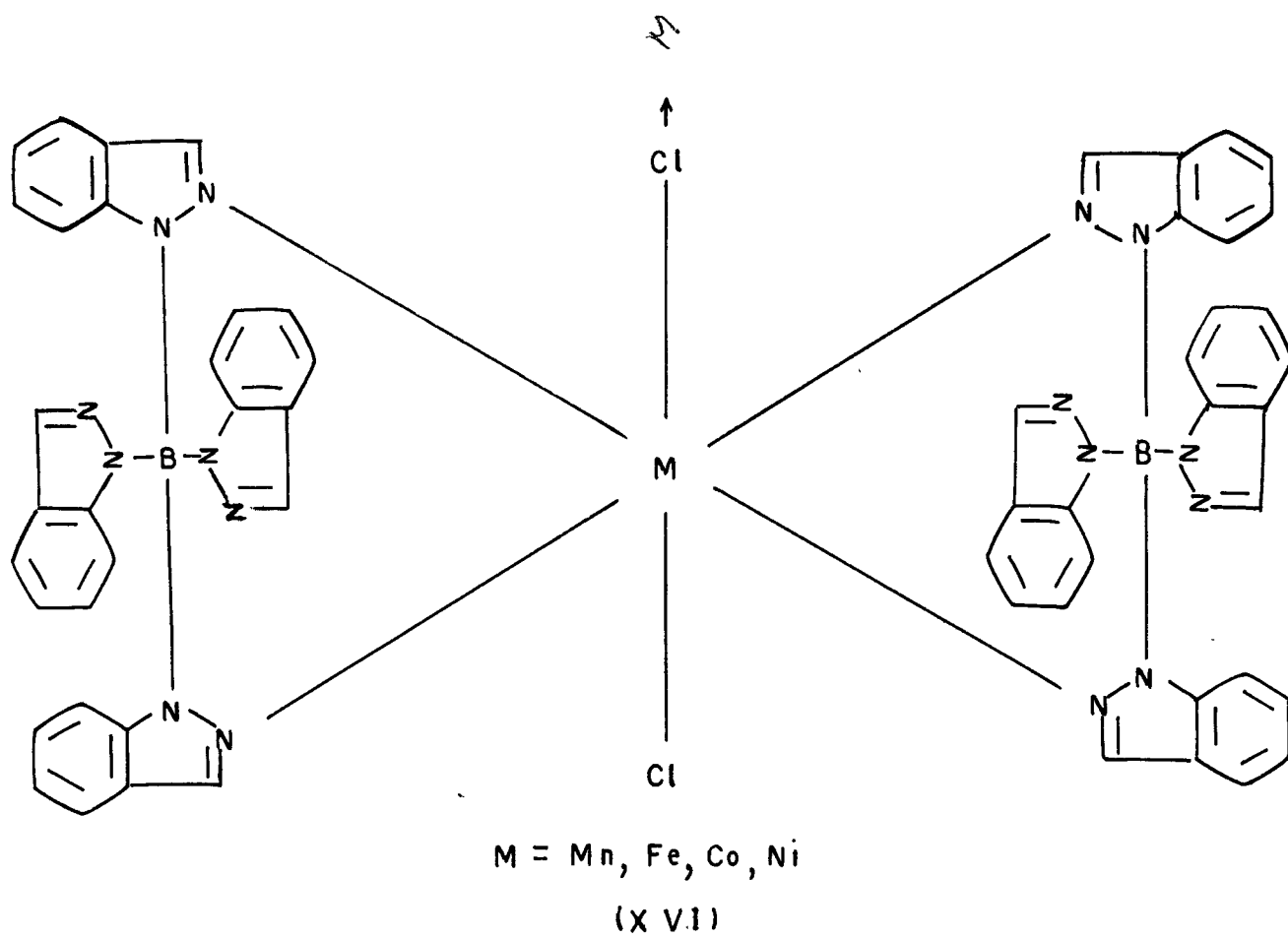


TABLE - VII

Analytical data, colour and melting points of potassium tetrakis(1-indazolyl) borate and its complexes

Complexes	Colour	M.p. ^o C	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Cl Found (Calcd)	% M Found (Calcd)
$(C_{28}N_8BH_{20})^{-}K^{+}$	Yellowish white	220 ^o C	63.5 (64.7)	3.6 (3.8)	20.8 (21.5)	-	-
$Cu[C_{28}N_8BH_{20}]Cl$	Green	>360 ^o C	60.3 (59.8)	3.1 (3.2)	18.5 (19.3)	7.5 (6.2)	11.6 (11.0)
$Ni[C_{28}N_8BH_{20}]Cl$	Light pink	>360 ^o C	59.4 (58.6)	2.8 (3.3)	20.3 (19.5)	5.8 (6.2)	10.8 (10.2)
$Co[C_{28}N_8BH_{20}]Cl$	Buff	>360 ^o C	57.6 (58.5)	3.5 (3.3)	19.6 (19.4)	7.2 (6.2)	10.5 (10.2)
$Mn[C_{28}N_8BH_{20}]Cl$	White	>360 ^o C	60.1 (59.0)	2.8 (3.3)	20.3 (19.6)	5.7 (6.3)	10.4 (9.6)
$Fe[C_{28}N_8BH_{20}]Cl$	Red	>360 ^o C	59.3 (58.9)	2.7 (3.3)	19.2 (19.6)	6.3 (6.1)	10.2 (9.8)

TABLE - VIII
I.R. Spectra of potassium tetrakis(1-indazolyl)borate and its complexes

Compound	$\nabla(B-H)$ cm^{-1}	Ring stretching cm^{-1}	$\nabla(C=N)$ cm^{-1}	$\nabla(M-N)$ cm^{-1}	$\nabla(M-Cl)$ cm^{-1}
$(C_{28}N_8BH_{20})^{-}K^{+}$	-	1608 s	1480 s	-	-
$Cu[C_{28}N_8BH_{20}]Cl$	-	1610 s	1485 s	380 s	290 m
$Ni[C_{28}N_8BH_{20}]Cl$	-	1615 s	1495 s	405 s	-
$Co[C_{28}N_8BH_{20}]Cl$	-	1615 s	1490 s	415 s	-
$Mn[C_{28}N_8BH_{20}]Cl$	-	1620 s	1505 s	390 s	-
$Fe[C_{28}N_8BH_{20}]Cl$	-	1618 s	1492 m	430 s	-

TABLE - IX

Molar conductance (Λ_M) values ($\text{ohm}^{-1} \text{ mole}^{-1} \text{ cm}^2$), electronic spectra and μ_{eff} values of complexes of potassium tetrakis(1-indazolyl)borate.

Compounds	μ_{eff} (B.M.)	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance		
				DMSO	DMF	Nitrobenzene
$\text{Cu}[\text{C}_{28}\text{N}_8\text{BH}_{20}]/\text{Cl}$	1.88	36,540		-	-	1.88
		34,210				
		24,410				
		19,210	$2A_{1g} \leftarrow$			
		13,920	$2E_g \leftarrow$ $2B_{1g}$ $2B_{1g}$			
$\text{Ni}[\text{C}_{28}\text{N}_8\text{BH}_{20}]/\text{Cl}$	2.87	36,560		-	1268	-
		34,220				
		21,600	$3T_1(P) \leftarrow$			
		14,520	$3T_{1g}(F) \leftarrow$			
		8,330	$3T_{1g}(F) \leftarrow$ $2g$			
$\text{Co}[\text{C}_{28}\text{N}_8\text{BH}_{20}]/\text{Cl}$	2.93	36,520		-	86.9	-
		34,220				
		27,240	Charge transfer			
		21,540	$4T_1(P) \leftarrow$			
		15,260	$4A_{2g}(F) \leftarrow$ $1g$			

..... contd

TABLE - IX: contd

Compounds	μ_{eff} (B.M.)	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance	
				DMSO	DMF Nitrobenzene
$\text{Mn} \left[\text{C}_{28}\text{N}_{18}\text{BH}_{20} \right] \text{Cl}$	5.90	36,530			
		34,440			
		25,230	$4A_1(B) \leftarrow$	42.8	-
		24,510	$4E_{1g}(G) \leftarrow$		
		18,670	$4T_{1g}(G) \leftarrow$ $6A_{1g}$ $6A_{1g}$ $6A_{1g}$		
$\text{Fe} \left[\text{C}_{28}\text{N}_{18}\text{BH}_{20} \right] \text{Cl}$	5.28	36,520			
		34,220			
		20,210		-	44.8
		15,250	$5E_g \leftarrow$		
		10,000	$5T_{2g}$		

CHAPTER - VI

SYNTHESIS OF POTASSIUM DIHYDROBIS (5-AMINOINDAZOLYL) BORATE AND ITS COMPLEXES

SYNTHESIS OF POTASSIUM DIHYDROBIS (5-AMINOINDAZOLYL) BORATE
AND ITS COMPLEXES

EXPERIMENTAL

Reagents used

5-Aminoindazole (Koch-light), m.p. 175°C was recrystallized from methanol. Cu(II), Ni(II), Co(II), Mn(II), Fe(III), Zn(II), Cd(II) and Hg(II) chlorides (All B.D.H., Reagents) were used as such.

Synthesis of potassium dihydrobis (5-aminoindazolyl)borate

Potassium borohydride (1 g) and 5-aminoindazole (9.85g) were mixed together in a 1:2 molar ratio and heated in a flat bottomed flask. 5-Aminoindazole was carefully melted by means of an oil bath at 180°C . When the contents of the flask was sufficiently molten to allow magnetic stirring, the mixture was stirred and heated at temperature not exceeding 180°C . Potassium borohydride reacted slowly with evolution of hydrogen which was collected over water. After 12 hours, 2 moles of hydrogen evolved and only a few small particles of KBH_4 were still left in the melt which were removed mechanically. The melt was poured into 250 ml, of toluene and the resulting mixture was stirred until it cooled to room tempe-

rature. It was then filtered and the solid so obtained was washed twice with hot toluene and recrystallized from hexane, m.p. 185-187°C. It was soluble in hexane as well as in ethyl alcohol.

Preparation of the complexes of dihydrobis(5-aminoindazolyl) borate

Dihydrobis(5-aminoindazolyl)borate copper(II): An alcoholic solution of copper(II) chloride(1 g) was added to ligand (1.27 g) solution in the same solvent. A dark blue solid product was obtained after standing the solution for few hours. It was filtered after twenty four hours and washed with absolute alcohol and dried in an oven at 100°C.

Dihydrobis(5-aminoindazolyl)borate nickel(II): This complex was prepared by the same procedure as described above. It yielded immediately a brownish red complex in cold.

Dihydrobis(5-aminoindazolyl)borate cobalt(II): The chocolate coloured cobalt complex of dihydrobis(5-aminoindazolyl)borate were prepared by mixing an absolute alcoholic solution of the ligand (1.31 g) with metal chloride (1 g). The precipitate appeared after keeping the mixture for few hours. It was filtered off, washed with ethanol and dried at 100°C.

Dihydrobis(5-aminoindazolyl)borate manganese(II): An alcoholic solution of potassium dihydrobis(5-aminoindazolyl) borate was added to Mn(II) chloride in an equimolar ratio, which gave a white solid after few hours.

Dihydrobis(5-aminoindazolyl)borate iron(III): When a solution of Fe(III) chloride (1 g) in 50 ml of ethyl alcohol was added to dihydrobis(5-aminoindazolyl)borate (2.51 g) in 100 ml of ethyl alcohol in 1:1 ratio it resulted in the formation of a white solid with greenish tinge. The product was isolated by filtration, washed thoroughly with alcohol, ether and dried in an oven at 100°C.

Dihydrobis(5-aminoindazolyl)borate zinc(II): Dihydrobis (5-aminoindazolyl)borate zinc(II) complex has been prepared by adding an alcoholic solution of zinc(II) chloride (1 g) to the ligand (2.31 g) in a 1:1 ratio. The complex was immediately obtained and digested on a waterbath for half an hour. It was filtered, washed with ethanol, ether and dried in vacuo.

Dihydrobis(5-aminoindazolyl)borate cadmium(II): This complex was prepared by adding an alcoholic solution of cadmium(II) chloride (1 g) to (1.73) dihydrobis(5-aminoindazolyl)borate. The white solid obtained was digested on a waterbath for one and a half hours, filtered, washed with

ethanol, ether and dried in an oven at 100°C.

Dihydrobis(5-aminoindazolyl)borate mercury(II): This white mercury (II) complex was prepared by mixing the ligand (1.73 g) with metal chloride (1 g) in absolute alcohol. The complex was obtained after standing for about four hours. It was washed as usual and dried in an oven.

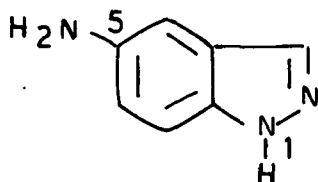
Results and Discussion

In the formation of potassium dihydrobis (5-aminoindazolyl)borate, the hydrogen atoms at position 1 in the 5-aminoindazole molecule are removed, together with the two hydrogen atoms of potassium borohydride, releasing two moles of hydrogen gas. The ligand has been characterized by the appearance of a strong multiplet at 2422 and 2385 cm^{-1} due to B - H stretch. The ∇ (N - H) could not be distinguished from ∇ (N-H) of primary amine even when the hydrogen at position 1 is removed in the form of hydrogen gas, because both appear nearly in the same region. The other characteristic frequencies of 5-aminoindazole reported earlier⁸⁷ also appear in the ligand. The ∇ (C = N) band at 1510 cm^{-1} and the ring stretching frequency at 1615 cm^{-1} are similar to those observed in the free indazole and 5-aminoindazole. The ligand was quite stable up to 100°C.

The analytical results of the complexes, their colour and melting points are given in table X. The experimental results are consistent with the theoretical values. All the complexes studied under this project, had a 1:2, metal:ligand ratio and were stable at room temperature. They are generally high melting solids, insoluble in usual organic solvents

except for a few which are sparingly soluble in dimethyl sulfoxide or dimethyl formamide or in nitrobenzene. The molar conductance in DMSO is lower than that required for a 1:1 electrolyte except for the dihydrobis (5-aminoindazolyl) borate manganese(II) complex, and the value of which suggests dissociation of the complex by the solvent molecules⁹⁹.

5-aminoindazole has three possible coordination sites namely; the pyridyl $\geq N$, pyrrole $>NH$ and the amino nitrogen - NH_2 atom¹⁰⁰.



(5-aminoindazole)
(XVII)

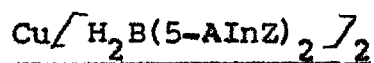
The i.r. spectral studies made on pyrazole and benzopyrazole complexes reveal very little change in group frequencies except for a marked shift in $\nu(N-H)$, when

compared with that of the free ligand^{34,48,92}. However, pyrazole is shown to coordinate through pyridyl nitrogen⁴⁸ but a clear cut assignment of ν (C = N) has not been made.

In the dihydrobis(5-aminoindazolyl)borate the ν (B - H) appears at 2385 and 2422 cm^{-1} but on complexation additional absorption bands have been observed (Table - XI). The metal nitrogen stretching frequency is in the 430-465 cm^{-1} range.

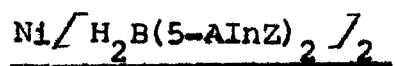
Electronic Spectra and Magnetic Susceptibilities

The electronic spectra of the complexes are summarized in table XII. The absorption bands observed in 36,440 cm^{-1} to 35,550 cm^{-1} and 34,430 cm^{-1} to 33,980 cm^{-1} ranges in all complexes (Table-XIII) are attributed to the ligand transition. A discussion of all the individual complexes is detailed below:



Cu(II) forms a 1:1 complex with potassium dihydrobis(1-indazolyl)borate⁹³ while the dihydrobis(5-aminoindazolyl)borate results in the formation of a 1:2 complex by the replacement of both the chlorine from Cu(II) chloride.

The reflectance spectrum shows absorption bands at $12,560 \text{ cm}^{-1}$ (${}^2T_{2g} \leftarrow {}^2E_g$) in addition to a weak band at $15,200 \text{ cm}^{-1}$ which may be due to spin forbidden transition. Its magnetic moment value ($\mu_{\text{eff}} = 1.75 \text{ B.M.}$) suggests it to have an octahedral geometry, like other Cu(II) complexes with similar ligands.



Poly(1-indazolyl)borate, $\left[\text{HnB}(\text{InZ})_{4-n} \right]$ (where $n = 1, 2, 3, 4$) complex of nickel(II) ion, $\text{Ni} \left[\text{HnB}(\text{InZ})_n \right] \text{Cl}$ is formed by the replacement of only one chlorine atom from nickel(II) chloride, whereas the corresponding dihydrobis (5-aminoindazolyl)borate yields a 1:2 complex, where both of the chlorine atoms from NiCl_2 are replaced by the ligand.

The reflectance spectrum shows absorption bands at $10,200 \text{ cm}^{-1}$, $17,500 \text{ cm}^{-1}$ and $29,300 \text{ cm}^{-1}$ assigned to

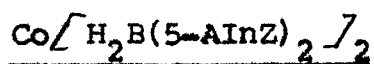


and



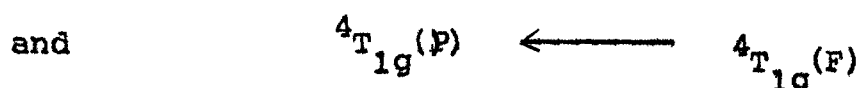
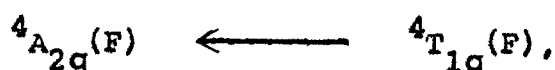
transitions respectively. The room temperature magnetic moment value ($\mu_{\text{eff}} = 2.90 \text{ B.M.}$) is in consonance with an

octahedral geometry for Ni(II) ion, which can be achieved only through ligand bridging in a polymeric fashion.

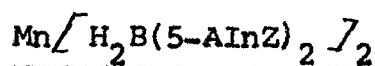


The dihydrobis(5-aminoindazolyl)borate complex of Co(II) differs from other Co(II) complexes of poly (1-indazolyl)borate in the sense that it has a higher magnetic moment value, which decides the stereochemistry of the complex.

The spectrum exhibits an absorption at $8,210 \text{ cm}^{-1}$, $17,230 \text{ cm}^{-1}$, and $19,850 \text{ cm}^{-1}$ assigned to

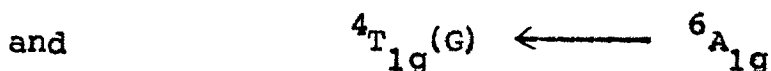
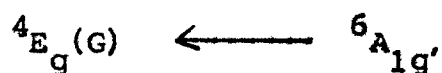
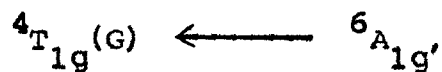


transitions respectively. The magnetic moment value of 4.95 B.M. for $\text{Co} \left[\text{H}_2\text{B}(5\text{-AInZ})_2 \right]_2$ is typical of an octahedral Co(II) complex in high spin state⁹⁰⁻⁹².

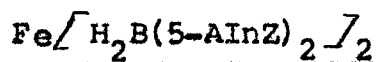


In the complex of dihydrobis(5-aminoindazolyl)borate manganese(II) the spectrum exhibits three bands at $25,550 \text{ cm}^{-1}$

24,210 cm^{-1} and 19,000 cm^{-1} assigned to



transition respectively. The room temperature magnetic moment value of 5.90 B.M. and electronic spectrum (Table-XII), suggests an octahedral geometry for $\text{Mn}[\text{H}_2\text{B}(\text{5-AInZ})_2]_2$ molecule.



The μ_{eff} value of 5.80 B.M. for the iron(II) complex as well as its electronic spectrum are consistent with an octahedral geometry about a high spin Fe(II) core. In the electronic spectrum of the Fe(II) complex the bands at 26,650 cm^{-1} must be attributed to charge transfer while only one band at around 10,110 cm^{-1} should be expected for the ${}^5\text{E}_g \longleftarrow {}^5\text{T}_{2g}$ transition in the case of Fe(II) ion having an octahedral geometry⁹⁶.

Dihydrotris(5-aminoindazolyl)borate zinc(II), dihydrobis
(5-aminoindazolyl)borate cadmium(II) and dihydrobis
(5-aminoindazolyl)borate mercury(II) .

All these complexes are diamagnetic. A comparison of the far I.R. spectra of the ligand and the above complexes reveals that a new band, not present in the ligand, appears at 410, 435 and 438 cm^{-1} for the zinc, cadmium and mercury complexes respectively. These must presumably be due to the M - N stretching vibrations suggesting coordination through the nitrogen atom.

The zinc, cadmium and mercury complexes may have an octahedral polymeric structure involving bridging through the ligand molecule.

TABLE - X

Analytical data, colour and melting points of potassium dihydrobis(5-aminoindazolyl) borate and its complexes

Complexes	Colour	M.p. ^o C	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% M Found (Calcd)
$\text{K}^+ \text{[H}_2\text{B(5-AInZ)}_2\text{]}^-$	Black	185-187 ^o C	53.6 (53.2)	4.3 (4.4)	25.8 (26.5)	-
$\text{Cu[} \text{H}_2\text{B(5-AInZ)}_2\text{]}_2$	Dark blue	254-255 ^o C	54.0 (54.8)	5.0 (4.5)	26.8 (27.4)	11.0 (10.2)
$\text{Ni[} \text{H}_2\text{B(5-AInZ)}_2\text{]}_2$	Brownish red	>360 ^o C	54.3 (55.2)	4.2 (4.6)	26.9 (27.6)	9.8 (9.5)
$\text{Co[} \text{H}_2\text{B(5-AInZ)}_2\text{]}_2$	Chocalate	>360 ^o C	54.8 (55.1)	4.3 (4.5)	28.8 (27.5)	10.2 (9.6)
$\text{Mn[} \text{H}_2\text{B(5-AInZ)}_2\text{]}_2$	White	>360 ^o C	56.2 (55.5)	4.9 (4.6)	26.8 (27.7)	10.5 (9.0)
$\text{Fe[} \text{H}_2\text{B(5-AInZ)}_2\text{]}_2$	White (greenish tinge)	>360 ^o C	56.8 (55.4)	3.8 (4.6)	28.5 (27.7)	10.8 (9.2)
$\text{Zn[} \text{H}_2\text{B(5-AInZ)}_2\text{]}_2$	White	>360 ^o C	55.2 (54.6)	3.9 (4.5)	28.5 (27.3)	11.8 (10.5)
$\text{Cd[} \text{H}_2\text{B(5-AInZ)}_2\text{]}_2$	White.	>360 ^o C	49.8 (50.6)	4.8 (4.2)	26.4 (25.3)	17.4 (16.9)
$\text{Hg[} \text{H}_2\text{B(5-AInZ)}_2\text{]}_2$	White	>360 ^o C	43.6 (44.7)	4.3 (3.7)	21.5 (22.3)	26.5 (26.7)

TABLE - XI
I.R. Spectra of potassium dihydrobis(5-aminoindazolyl)borate and its complexes.

Compound	$\text{B} - \text{H}$ cm^{-1}	Ring stretching cm^{-1}	$\text{C} = \text{N}$ cm^{-1}	$\text{M} - \text{N}$ cm^{-1}
$\text{K}^+ \text{H}_2\text{B}(\text{5-AInZ})_2$	2422 m, sh 2385 w	1615 s	1510 s	-
$\text{Cu} \text{H}_2\text{B}(\text{5-AInZ})_2$	2420 m, sh 2370 w	1612 s	1500 s	430 s
$\text{Ni} \text{H}_2\text{B}(\text{5-AInZ})_2$	2410 m 2360 w	1610 s	1510 s	425 s
$\text{Co} \text{H}_2\text{B}(\text{5-AInZ})_2$	2415 m, sh 2470 m	1620 s	1520 s	435 s
$\text{Mn} \text{H}_2\text{B}(\text{5-AInZ})_2$	2420 m, sh 2340 m	1615 s	1510 s	465 s
$\text{Fe} \text{H}_2\text{B}(\text{5-AInZ})_2$	2420 m 2370 w	1615 s	1510 s	435 s
$\text{Zn} \text{H}_2\text{B}(\text{5-AInZ})_2$	2410 m, sh 2380 w	1610 s	1500 s	410 s
$\text{Cd} \text{H}_2\text{B}(\text{5-AInZ})_2$	2420 m, sh 2380 w	1610 s	1520 s	435 s
$\text{Hg} \text{H}_2\text{B}(\text{5-AInZ})_2$	2415 m, sh 2380 m	1620 s	1500 s	438 s

TABLE - XII

Molar conductance (Λ_M) values ($\text{ohm}^{-1} \text{ mole}^{-1} \text{ cm}^2$), electronic spectra and μ_{eff} values of complexes of potassium dihydrobis(5-aminoindazolyl)borate

Compounds	μ_{eff} (B.M.)	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance		
				DMSO	DMF	Nitrobenzene
$\text{Cu}[\text{H}_2\text{B}(\text{5-AInZ})_2]_2$	1.75	35,860	$2T_{2g} \leftarrow 2E_g$	-	-	89.4
		34,430				
		15,200				
		12,560				
$\text{Ni}[\text{H}_2\text{B}(\text{5-AInZ})_2]_2$	2.90	36,200	$3T_1(P) \leftarrow 3A_2(F)$ $3T_1(F) \leftarrow 3A_2(F)$ $3T_1(F) \leftarrow 3A_2(F)$	-	-	92.5
		33,980				
		29,300				
		17,500				
		10,200				
$\text{Co}[\text{H}_2\text{B}(\text{5-AInZ})_2]_2$	4.95	34,220	$4T_1(P) \leftarrow 4T_{1g}(F)$ $4A_{1g}(F) \leftarrow 4T_{1g}(F)$ $4T_{2g}(F) \leftarrow 4T_{1g}(F)$	-	90.1	
		19,850				
		17,230				
		8,210				
$\text{Mn}[\text{H}_2\text{B}(\text{5-AInZ})_2]_2$	5.90	35,550	$4T_1(G) \leftarrow 6A_{1g}$ $4E_{1g}(G) \leftarrow 6A_{1g}$ $4T_{1g}(G) \leftarrow 6A_{1g}$		44.8	
		25,550				
		24,210				
		19,000				

..... contd

TABLE - XII: contd

Compounds	μ_{eff} (B.M.)	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance		
				DMSO	DMF	Nitrobenzene
$\text{Fe} / \text{B}_2\text{B}(5\text{-AInZ})_2 / 2$	5.80	36,440	$5\text{E}_g \leftarrow 5\text{T}_{2g}$	64.7	-	-
		34,000				
		26,650				
		15,560				
		10,110				
$\text{Zn} / \text{H}_2\text{B}(5\text{-AInZ})_2 / 2$	-	-	-	70.00	-	-
$\text{Cd} / \text{H}_2\text{B}(5\text{-AInZ})_2 / 2$	-	-	-	-	87.9	-
$\text{Hg} / \text{H}_2\text{B}(5\text{-AInZ})_2 / 2$	-	-	-	-	88.9	-

CHAPTER - VII

SYNTHESIS OF POTASSIUM HYDROTRIS(5-AMINOINDAZOLYL) BORATE AND ITS COMPLEXES

SYNTHESIS OF POTASSIUM HYDROTRIS(5-AMINOINDAZOLYL) BORATE AND
ITS COMPLEXES

Synthesis of potassium hydrotris(5-aminoindazolyl)borate

Potassium borohydride (1g) and 5-aminoindazole (9.85g) were mixed together in a 1:3 molar ratio in a flask and heated gently. This mixture was kept in an oil bath at 195°C until the contents were sufficiently molten. The mixture was then stirred and heated at temperature not exceeding 200°C. Potassium borohydride reacted slowly with evolution of hydrogen which was collected over water. Three moles of hydrogen had evolved after 12 hours leaving behind a trace of potassium borohydride which were removed from the melt. The melt was poured into a flask containing 250 ml of toluene. The resulting mixture was stirred until it cooled to room temperature. It was then filtered and the solid so obtained was washed twice with hot toluene and recrystallized from hexane m.p. 205°C.

Preparation of potassium hydrotris(5-aminoindazolyl)borate complexes

Hydrotris(5-aminoindazolyl)borate copper(II)

A solution of copper(II) chloride (1 g) in 200 ml of absolute alcohol was added to ligand (2.67 g) in 100 ml of

absolute alcohol, which, after stirring for few hours, gave a dark blue solid. The complex was digested on a water bath for an hour and then filtered and washed with alcohol and dried in an oven at 100°C.

Hydrotris(5-aminoindazolyl)borate nickel(II)

This complex was prepared by the procedure described above for Cu(II) compound by adding alcoholic solution of nickel chloride (1 g) to the ligand (1.88 g) solution.

Hydrotris(5-aminoindazolyl)borate cobalt(II)

It was prepared by mixing an absolute alcoholic solution of the ligand (1.87 g) with metal chloride (1 g) at room temperature. The precipitate appeared slowly after standing the solution for few hours. It was filtered off, washed with ethanol and dried at 100°C.

Hydrotris(5-aminoindazolyl)borate manganese(II)

This light yellow solid was prepared in the same manner as described for nickel (II) complex. of manganese(II) chloride was added to the ligand in the same solvent. A solid appeared after keeping this mixture for about two hours. The solid thus obtained was filtered, washed with ethanol and dried at 100°C.

Hydrotris(5-aminoindazolyl)borate iron(II)

An immediate precipitation occurred when the ligand (3.55 g) and the metal chloride (1 g) were mixed together in cold. The solid thus obtained was digested on a water bath, filtered, washed several times with alcohol and ether and dried in vacuum. The white (greenish tinge) solid was insoluble in usual organic solvents.

Hydrotris(5-aminoindazolyl)borate zinc(II)

An alcoholic solution of the ligand (3.28 g) was added to zinc chloride (1 g) in the same solvent ratio. A white solid thus obtained was dried in vacuo.

Hydrotris(5-aminoindazolyl)borate cadmium(II)

This compound was prepared by adding cadmium(II) chloride (1 g) to a continuously stirred alcoholic solution of potassium hydrotris(5-aminoindazolyl)borate (2.44g). The precipitate was filtered and purified further by recrystallization from alcohol.

Hydrotris(5-aminoindazolyl)borate mercury(II)

An alcoholic solution of the ligand (1.89 g) was added to mercury(II) chloride (1 g) in the same solvent. A solid which appeared immediately, was filtered off, washed with ethanol and ether and dried at 100°C.

Results and Discussion

The composition of potassium hydrotris (5-aminoindazolyl)borate was confirmed by elemental analysis and by the appearance of $\nu(\text{B-H})$ band at 2420 cm^{-1} confirming that three hydrogen atoms have been replaced. Since the $\nu(\text{N-H})$ could not be distinguished from $\nu(\text{N-H})$ of primary amine even when the hydrogen at position 1 is removed in the form of hydrogen gas as they both appear nearly in the same region. The other characteristic frequencies of 5-aminoindazole also appear in the ligand⁸⁷. The ligand was quite stable up to 100°C . The $\nu(\text{C}=\text{N})$ and the ring stretching frequencies appearing at 1500 cm^{-1} and 1620 cm^{-1} respectively are not much different from that of the free 5-aminoindazole and potassium dihydrobis (5-aminoindazolyl)borate.

The analytical results of the complexes suggest a 1:2, metal:ligand ratio. These high melting solids are fairly stable at room temperature. Most of these complexes are insoluble, except for a few which dissolve in nitrobenzene or dimethyl formamide or dimethyl sulfoxide. Though the conductance in dimethyl sulfoxide medium is slightly higher, these are however not as high as required for 1:1 electrolytes except in the case of hydrotris(5-aminoindazolyl)borate

manganese(II) complex.

The change in the I.R. spectrum on going from free to complexed ligand is unusual. The ligand ring frequency at 1620 cm^{-1} shifts to somewhat lower frequency on complexation (Table-XIV). The M-N stretching frequency lies in the $410\text{--}450\text{ cm}^{-1}$ range (Table-XIV).

Electronic spectra and Magnetic Susceptibilities

The electronic spectra of the metal complexes of hydrotris(1-indazolyl)borate have been summarized in table XIV. Since the bands observed in the range $36,460$ to $36,210\text{ cm}^{-1}$ and $34,550$ to $34,220\text{ cm}^{-1}$ appear in all the complexes (Table-XVI) they are attributed to ligand transitions.

In the case of hydrotris(1-pyrazolyl)borate complexes with divalent metal halides all the halogens have been replaced by the ligand giving a 1:2 complex and that the coordination behaviour of hydrotris(5-aminoindazolyl)borate is similar to the above ligand^{27,40,56}.

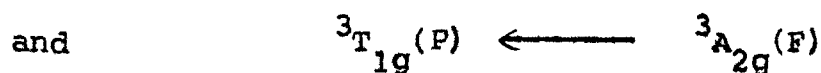
An individual discussion of all the complexes is detailed below.

$\text{Cu} / \text{HB}(5\text{-AInZ})_3 /_2$

The electronic spectrum of $\text{Cu} / \text{HB}(5\text{-AInZ})_3 /_2$ shows absorption bands at $12,430 \text{ cm}^{-1}$ (${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$) in addition to a weak band at $15,250 \text{ cm}^{-1}$ which may be due to spin forbidden transition. Its magnetic moment value (1.74 B.M.) suggests it to have an octahedral geometry as has been found in several Cu(II) complexes with similar type of ligands^{40,56,105}.

$\text{Ni} / \text{HB}(5\text{-AInZ})_3 /_2$

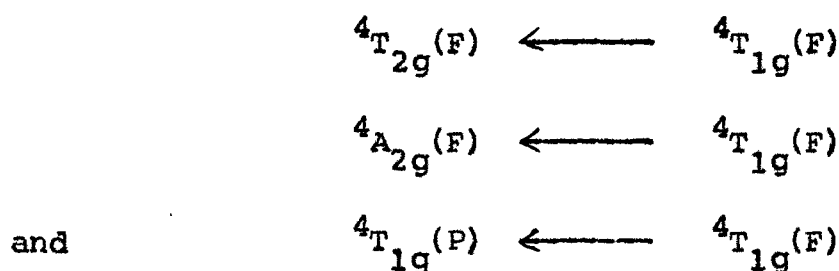
The nickel complex shows three bands at 10,210, 17,660, and $29,330 \text{ cm}^{-1}$ assignable to



transitions for an octahedral nickel(II) ion¹⁰⁰. The room temperature magnetic moment value ($\mu_{\text{eff}} = 2.90 \text{ B.M.}$) is also in consonance with the proposed geometry, which can be achieved only through ligand bridging.

Co[HB(5-AInZ)₃]₂

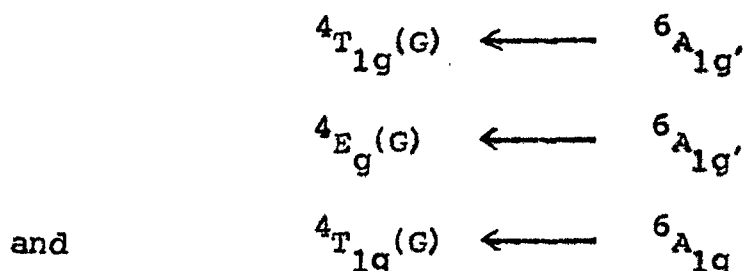
The reflectance spectrum exhibits an absorption at 8,200 cm⁻¹, 17,340 cm⁻¹ and at 19,800 cm⁻¹ assigned to



transitions respectively. The magnetic moment^{93,95} value of 4.92 B.M for Co²⁺ ion in Co[HB(5-AInZ)₃]₂ is typical of an octahedral Co⁺² complex in high spin state⁹⁰⁻⁹².

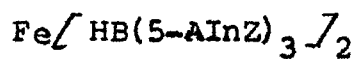
Mn[HB(5-AInZ)₃]₂

The manganese complex shows three bands at 19,210 cm⁻¹, 24,210 cm⁻¹ and 25,220 cm⁻¹ assignable to



transitions respectively. The room temperature magnetic moment value (5.88 B.M) and its electronic spectrum (Table - XV) suggests an octahedral geometry for manganese(II)

ion in this complex.



The μ_{eff} value for the iron(II) complex as well as its electronic spectrum are consistent with an octahedral geometry about a high spin Fe(III) core. In the electronic spectrum of the Fe(II) complex the bands at $26,650 \text{ cm}^{-1}$ must be attributed to the charge transfer, While only one band at around $10,200 \text{ cm}^{-1}$ should be expected for the ${}^5\text{E}_g \longleftarrow {}^5\text{T}_{2g}$ transition in the case of Fe(II) ion having an octahedral geometry⁹⁶.

Hydrotris(5-aminoindazolyl)borate zinc(II), hydrotris(5-aminoindazolyl)borate cadmium(II) and hydrotris(5-aminoindazolyl)borate mercury(II).

There is a positive shift in C = N stretching vibration in all the above complexes indicating coordination through the nitrogen atom.

A comparison of the far I.R. spectra of the ligand and the above complexes reveals that a new band, not present in the ligand, appears at 410, 430 and 435 cm^{-1} for the zinc, Cadmium and mercury complexes respectively. These must presumably be due to M-N stretching vibrations. All these complexes are diamagnetic.

TABLE - XIII

Analytical data, colour and melting points of potassium dihydrotris(5-aminoindazolyl) borate and its complexes

Complexes	Colour	M.p. ^o C	% C		% H		% N		% M	
			Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)
$\text{[HB(5-AInZ)}_3\text{]}^+\text{K}^+$	Black	205 ^o C	60.6 (60.8)	5.2 (5.0)	30.8 (30.6)	-	-	-	-	-
$\text{Cu[HB(5-AInZ)}_3\text{]}_2$	Dark blue	270-272 ^o C	55.8 (56.3)	4.4 (4.2)	27.5 (28.1)	8.3 (7.2)	-	-	-	-
$\text{Ni[HB(5-AInZ)}_3\text{]}_2$	Lilac	>360 ^o C	57.2 (58.0)	4.4 (4.3)	28.5 (29.0)	7.2 (6.7)	-	-	-	-
$\text{Co[HB(5-AInZ)}_3\text{]}_2$	Chocalate	>360 ^o C	58.5 (58.3)	4.6 (4.3)	28.8 (29.1)	6.9 (6.8)	-	-	-	-
$\text{Mn[HB(5-AInZ)}_3\text{]}_2$	Light yellow	>360 ^o C	58.9 (58.6)	4.6 (4.4)	28.2 (29.3)	6.9 (6.3)	-	-	-	-
$\text{Fe[HB(5-AInZ)}_3\text{]}_2$	White (greenish) tinge	>360 ^o C	59.0 (58.5)	4.2 (4.4)	28.5 (29.2)	6.2 (6.5)	-	-	-	-
$\text{Zn[HB(5-AInZ)}_3\text{]}_2$	White	>360 ^o C	58.2 (57.9)	5.1 (4.3)	29.5 (28.9)	8.2 (7.4)	-	-	-	-
$\text{Cd[HB(5-AInZ)}_3\text{]}_2$	White	>360 ^o C	55.2 (54.9)	5.0 (4.1)	28.3 (27.4)	12.5 (12.2)	-	-	-	-
$\text{Hg[HB(5-AInZ)}_3\text{]}_2$	White	>360 ^o C	50.8 (50.1)	3.5 (3.7)	25.1 (25.0)	19.2 (19.9)	-	-	-	-

TABLE - XIV

I.R. Spectra of potassium hydrotris(5-aminoindazolyl)borate and its complexes.

Compound	ν B - H cm^{-1}	Ring stretching cm^{-1}	ν C = N cm^{-1}	ν M - N cm^{-1}
$\text{[HB(T-AInZ)}_3\text{]}^{\text{K}^+}$	2420 m	1620 s	1500 s	-
$\text{Cu[HB(5-AInZ)}_3\text{]}_2$	2370 b	1620 s	1510 s	425 s
$\text{Ni[HB(5-AInZ)}_3\text{]}_2$	2370 b	1620 s	1512 s	410 s
$\text{Co[HB(5-AInZ)}_3\text{]}_2$	2420 m, sh	1610 s	1510 s	440 s
$\text{Mn[HB(5-AInZ)}_3\text{]}_2$	2435 m, sh	1615 s	1515 s	445 s
$\text{Fe[HB(5-AInZ)}_3\text{]}_2$	2390 b	1620 s	1520 s	450 s
$\text{Zn[HB(5-AInZ)}_3\text{]}_2$	2420	1610 s	1510 s	410 s
$\text{Cd[HB(5-AInZ)}_3\text{]}_2$	2415 m, sh	1615 s	1500 s	430 s
$\text{Hg[HB(5-AInZ)}_3\text{]}_2$	2370 m, sh	1620 s	1510 s	435 s

TABLE - XV

Molar conductance (Λ_M) value ($\text{ohm}^{-1} \text{ mole}^{-1} \text{ cm}^2$), electronic spectra and μ_{eff} values of complexes of potassium hydrotris(5-aminoindazolyl)borate

Compounds	μ_{eff} (B.M.)	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance		
				DMSO	DMF	Nitrobenzene
$\text{Cu}[\text{HB}(5\text{-AInZ})_3]_2$	1.74	36,220	$2T_{2g} \leftarrow 2E_g$	-	-	92.8
		34,440				
		15,250				
		12,430				
$\text{Ni}[\text{HB}(5\text{-AInZ})_3]_2$	2.90	36,460	$3T_1(P) \leftarrow 3A_2(F)$ $3T_1(F) \leftarrow 3A_2(F)$ $3T_1(F) \leftarrow 3A_2(F)$	-	66.9	-
		34,430				
		29,330				
		17,660				
		10,210				
$\text{Co}[\text{HB}(5\text{-AInZ})_3]_2$	4.92	36,220	$4T_1(P) \leftarrow 4T_{1g}(F)$ $4A_{1g}(F) \leftarrow 4T_{1g}(F)$ $4T_{2g}(F) \leftarrow 4T_{1g}(F)$	-	86.9	-
		34,220				
		19,800				
		17,340				
		8,200				
$\text{Mn}[\text{HB}(5\text{-AInZ})_3]_2$	5.88	34,550	$4T_1(G) \leftarrow 6A_{1g}$ $4E_g(G) \leftarrow 6A_{1g}$ $4T_1(G) \leftarrow 6A_{1g}$	42.8	-	-
		25,220				
		24,210				
		19,210				

..... contd

TABLE - XV : contd

Compounds	μ_{eff} (B.M.)	Electronic bands (cm^{-1})	Assignment of Transition	Molar conductance	
				DMSO	DMF Nitrobenzene
$\text{Fe} \begin{array}{c} \diagup \\ \text{HB}(5\text{-AlInZ})_3 \end{array} \diagdown_2$	5.80	36,210	$5E_g \longleftarrow 5T_{2g}$	68.3	-
		34,410			
		15,520			
		10,200			
$\text{Zn} \begin{array}{c} \diagup \\ \text{HB}(5\text{-AlInZ})_3 \end{array} \diagdown_2$	-	-	-	69.8	-
$\text{Cd} \begin{array}{c} \diagup \\ \text{HB}(5\text{-AlInZ})_3 \end{array} \diagdown_2$	-	-	-	- 89.3	-
$\text{Hg} \begin{array}{c} \diagup \\ \text{HB}(5\text{-AlInZ})_3 \end{array} \diagdown_2$	-	-	-	- 87.4	-

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